

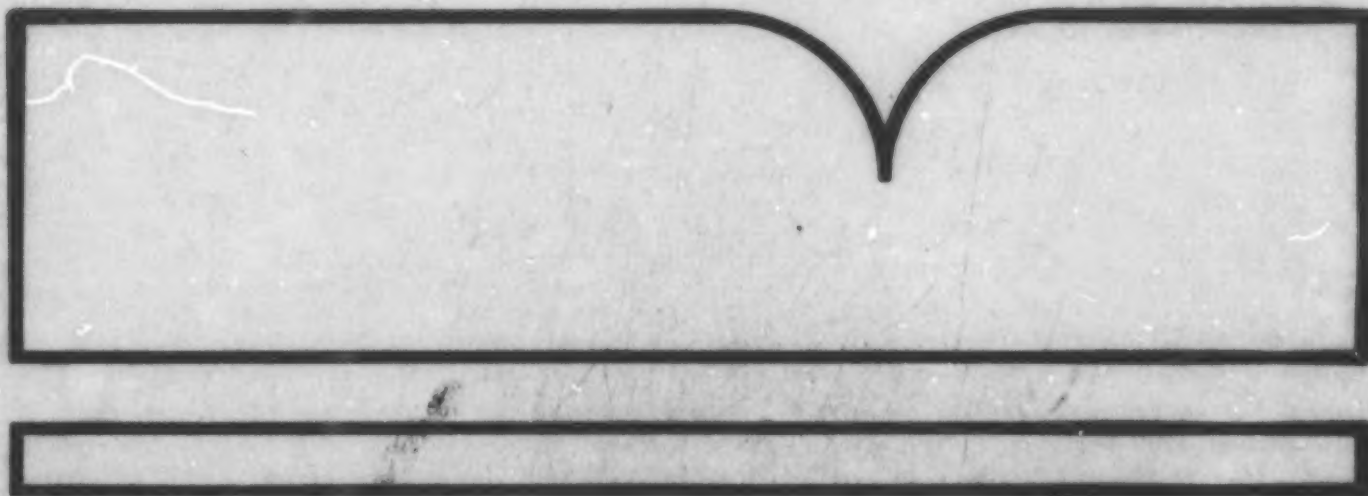
Characterization of Scrubbed and
Unscrubbed Power Plant Plumes

Meteorology Research, Inc.
Santa Rosa, CA

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Jun 81



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CHARACTERIZATION OF SCRUBBED AND UNSCRUBBED
POWER PLANT PLUMES

by

Gregory R. Markowski
Jeffrey L. Stith
L. Willard Richards

Meteorology Research, Inc.
3402 Mendocino Avenue
Santa Rosa, California 95401

EPA Contract No. 68-02-3418

Project Officer

Harold M. Barnes
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

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ABSTRACT

Airborne measurements of scrubbed and unscrubbed plumes from the Widows Creek Steam Plant were made during August 17 to 25, 1978, under the SCRUB program. Data from the flight program (except size distribution data) and preliminary data analysis results have been previously published in a Data Volume.

This report briefly describes the flight program and methodology of the SCRUB program and gives the results of the analysis of the data gathered during the flight program. The analysis results cover plume chemistry, primary aerosol, aerosol size distributions, and aerosol formation rates among the scrubbed and mixed plumes.

Little difference was seen in photochemical aerosol and sulfate formation in the scrubbed and unscrubbed plumes. However, measurement noise and plume mixing may have obscured moderate differences. The submicron primary emissions from the scrubbed unit were only about 14 percent of those from the unscrubbed unit.

Sulfur dioxide to sulfate conversion rates in the plumes were between 0 and 3.2 percent per hour. Aerosol formation rates varied between 0 and 0.30 microns³/(ppb SO₂ - hr - cm³). More sulfate was measured than could be accounted for by the aerosol measurements.

Ozone bulges of 40 ppb were typical in the afternoon 50 kilometers downwind of the plant.

Photochemical reactions were most rapid when the plume was dilute and the sunlight strong.

Submicron primary emissions from all units appeared to be mostly sulfuric acid.

This report was submitted in fulfillment of Contract No. 68-02-3418 by Meteorology Research, Inc., under the sponsorship of the U.S. Environmental Protection Agency.

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CONTENTS

Disclaimer	ii
Abstract	iii
Figures	vi
Tables	vii
Acknowledgments	viii
1. Purpose and Background	1
Purpose	1
Background	1
Widows Creek Steam Plant Configuration	2
2. Conclusions and Recommendations	4
Conclusions	4
Recommendations	6
3. Instrumentation, Data Collection Methods, and Flights	8
The Widows Creek Steam Plant	8
Data Collection: Instrumentation and Methodology	8
Summary of Sampling Program	13
4. Daily Weather and Flight Summary	16
August 17	16
August 19	17
August 21	17
August 22	17
August 23	18
August 25	18
5. Photochemical Aerosol Formation in the Widows Creek Plume	19
Sulfate Measurements	19
Sulfate Formation Rates	23
Aerosol Formation	26
Comparison of Sulfate and Aerosol Formation Results	35
6. Primary Sulfuric Acid	38
Measurements, Calculations, and Assumptions	38
Primary Sulfuric Acid	39
Comparison of the Scrubbed and Unscrubbed Units	44
7. Gas Chemistry	45
Ozone Bulges	45
NO _x Depletion	45
Near Source NO ₂	47
References	48

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FIGURES

<u>Number</u>		<u>Page</u>
1	Schematic of TVA's Widows Creek Power Plant	3
2	MRI Queen Air sample inlet lines and external probes	12
3	Comparison of sulfur concentrations from ion chromato- graphic analysis of RSP filters and Particle Induced X-Ray Emission (PIXE) analysis of Lundgren Impactor samples	21
4	Comparison of sulfur concentrations from ion chromato- graphic analysis of RSP filters and flash volatiliza- tion/flame photometric analysis of Two-Mass filters	
5	Average plume and background aerosol size distribu- tion during a period of maximum aerosol formation: noon, August 23, 1978, 50 km downwind	30
6	Average plume and background aerosol size distribu- tion during a period of maximum aerosol formation: 1230 CST, August 25, 1978, 50 km downwind	31
7	Plume and background plus primary aerosol distribu- tions 9 kilometers from Widows Creek Station, August 17, 1978	34
8	Plume excess aerosol distribution from Unit 8 at 0.5 km downwind compared to expected fly ash distribution	42
9	Plume excess aerosol distribution from Units 7 and 8 at 0.5 km downwind compared to expected fly ash distribution	43

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TABLES

<u>Number</u>		<u>Page</u>
1	Queen Air instrumentation	9
2	SCRUB program summary	14
3	In plume sulfate formation based on filter measurements	24
4	Aerosol growth rate calculations	28
5	Nuclei and accumulation mode volume concentrations	32
6	Comparison of sulfate and aerosol measurements	36
7	Primary flue gas sulfuric acid	40
8	Ozone bulges	46

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The assistance and helpful suggestions of Dr. Pete McMurry (University of Minnesota) and Dr. Jim Meagher (Tennessee Valley Authority) contributed significantly to the work.

The authors are grateful to Jerry Anderson, Don Blumenthal, Sandy McDonald, and John Ogren who planned the field program and made the measurements.

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SECTION 1

PURPOSE AND BACKGROUND

PURPOSE

The purpose of the study "Characterization of Scrubbed and Unscrubbed Power Plant Plumes" (referred to as the SCRUB project) was to investigate differences in photochemical processes in scrubbed and unscrubbed power plant plumes. This report briefly describes the flight program and methodology of the SCRUB program and gives the results of the analysis of the data gathered during the flight program. The analysis results cover plume chemistry, primary aerosol, aerosol size distributions, and aerosol formation rates among the scrubbed and mixed plumes.

Data from the flight program (except size distribution data) and preliminary data analysis results have been published in a Data Volume (Stith, et al., 1979a) and an Interim Report (Stith et al., 1979b), respectively. The Interim Report contains plume profiles of condensation nuclei, light scattering coefficient, ozone, and SO₂ concentrations at varying downwind distances and days that are not included in this report.

BACKGROUND

The production of primary and secondary pollutants has been studied extensively in plumes of unscrubbed power plants, but only preliminary work has been done to determine the effects of scrubbers on downwind plume chemistry. There is mounting political pressure to reduce ambient sulfate levels by reducing the coal-fired power plant emissions of sulfur dioxide (SO₂), which is the precursor to secondary sulfate particles (produced by gas-to-particle conversion). The primary methods of reducing SO₂ emissions are to use low sulfur coal or to use scrubbers before the stack. Since scrubbing allows the use of higher sulfur coal, scrubbing is likely to become more common in the future as utilities use the more available higher sulfur coal.

A number of studies have been conducted to determine the rate of gas-to-particle conversion in the atmosphere. A recent review by Hegg (1979) lists the results of 11 separate investigations of the conversion rates of sulfur dioxide; conversion rate estimates in these studies range from 0 - 30 percent hr⁻¹. However, most recent studies (e.g., Forrest and Newman, 1977; Ursenbach et al., 1977; Cantrell and Whitby, 1978; Gillani et al., 1978; Husar et al., 1978; Pueshell and Van Valin, 1978; Stith, 1978; Hegg, 1979) indicate a conversion rate between 0 and 10 percent hr⁻¹.

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In spite of the many studies of gas-to-particle conversion rates which have been conducted, there still exists considerable uncertainty as to the formation mechanisms, and the rates of conversion. Husar et al. (1978) and Gillani et al. (1978) have observed sulfate conversion to be directly related to the amount of solar radiation for the coal-fired Labadie Power Plant. Cantrell and Whitby (1978), also at the Labadie plant, found the sulfate fraction to monotonically increase with plume travel time. On the other hand, Forrest and Newman (1977) and Meagher et al. (1978a) found very little change in secondary sulfates with plume travel time. Friberg (1978) suggested that conversion proceeds to a fractional asymptotic limit.

Dittenhoffer and De Pena (1978) found the production of Aitken particles, in the Keystone coal-fired power plant, to be the dominant secondary production process under conditions of low humidity, near neutral stability, and strong solar radiation; while for plumes of relative humidity near 100 percent, they found that conversion occurred on pre-existing droplets.

In a study of the Labadie Power Plant, Whitby et al. (1978) found the creation of nuclei mode particles to range from about $1700 \text{ cm}^{-3}\text{s}^{-1}$ (at 6:30 in the morning) to about $1 \text{ cm}^{-3}\text{s}^{-1}$ at night. They found that about 5 percent of the aerosol volume which formed as a result of gas-to-particle conversion went into the nuclei mode, and this ratio was independent of the conversion rate. They also found that coagulation of these nuclei with particles in the accumulation ($0.05 - 1.0 \mu\text{m}$) mode reduced the mean size of particles in the accumulation mode in the plumes as compared to the background air.

One of the main mechanisms for the oxidation of SO_2 (as well as NO_2) is oxidation by OH radicals. The rate of oxidation by this mechanism is between $0.4 - 2.7 \text{ percent hr}^{-1}$ for SO_2 (Calvert et al., 1978) and about $13 \text{ percent hr}^{-1}$ for NO_2 (Cox, 1974). Since the OH radicals are formed photochemically, the rate of conversion should depend on the amount of solar radiation.

SO_2 oxidation may also take place on the surface of existing particles (e.g., carbon particles) or in water droplets. This liquid phase oxidation may play an important role under cloudy or high humidity conditions (Hegg and Hobbs, 1978). Further, metal salts in fly ash act as catalysts for the oxidation of SO_2 dissolved in water droplets. Thus, the SO_2 conversion rates may be affected by any droplets produced by the scrubber.

WIDOWS CREEK STEAM PLANT CONFIGURATION

Figure 1 is a schematic diagram of the control devices and stacks of the Widows Creek Steam Plant, and is presented here to help the reader understand the conclusions and recommendations which follow. Additional information on the plant is given at the beginning of Section 3.

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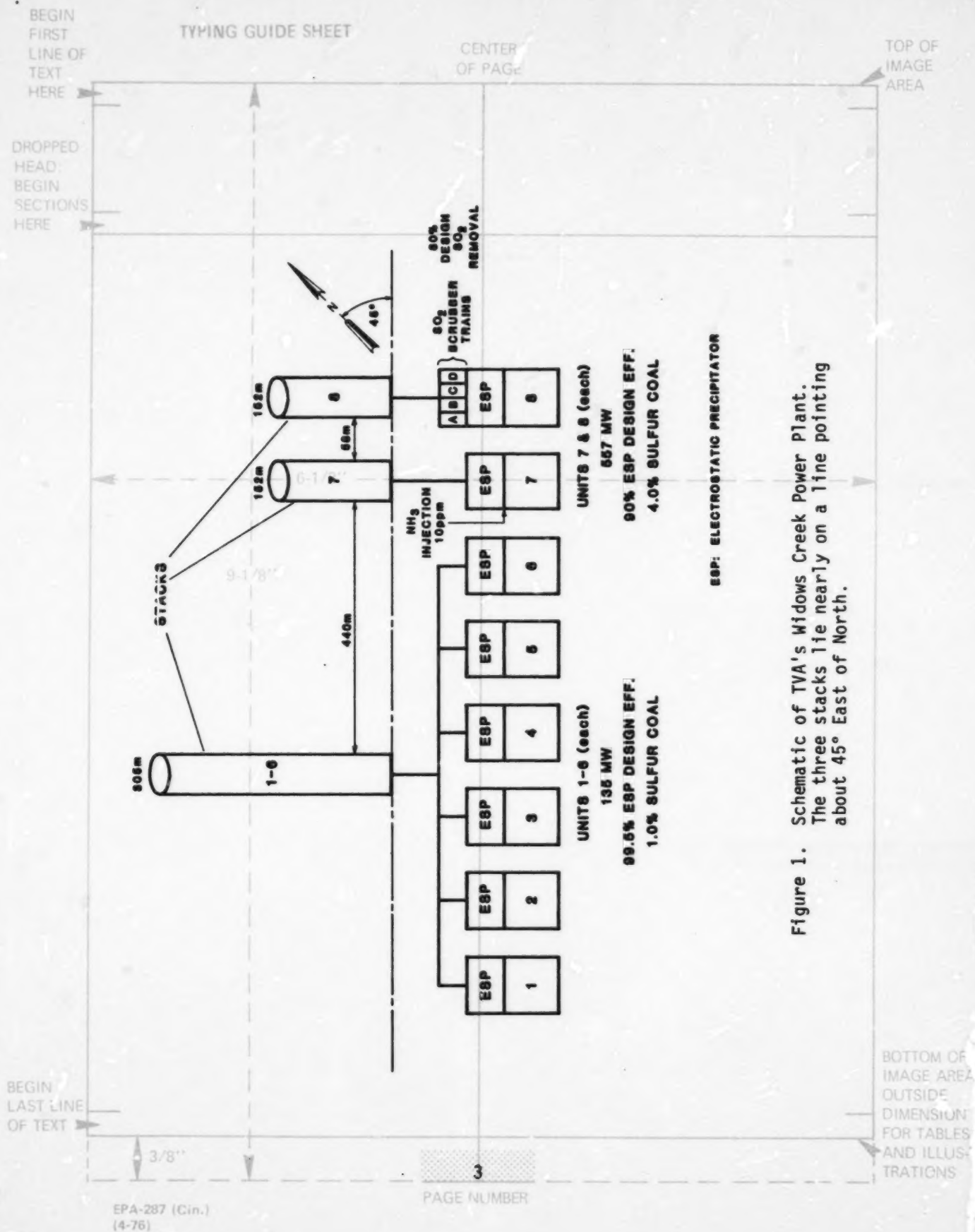


Figure 1. Schematic of TVA's Widows Creek Power Plant.
The three stacks lie nearly on a line pointing
about 45° East of North.

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SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Comparison of Scrubbed and Unscrubbed Plumes

- 1) Summary: No significant differences were seen between the scrubbed and unscrubbed plumes. Differences may have been obscured because the plumes were usually mixed.
- 2) Plume Separation: Plumes sampled more than 1 km downwind were nearly always mixed plumes from all operating units. Unit 7 was not operating during flights on August 17, 22 and 23.
- 3) Plume Separation: Plumes sampled at 0.5 km were a mixture of plumes from Units 7 and 8 only, except when Unit 7 was not operating.
- 4) Photochemistry. Nearly identical ozone bulges, about 40 ppb, were seen 50 km downwind both when Unit 7 was and was not in operation. The unscrubbed Unit 7 increased the total sulfur in the mixed plume by a factor of about 2.5.
- 5) Aerosol Formation: Aerosol formation rates, expressed as percent per hour SO₂ conversion, were nearly identical when Unit 7 was and was not operating. Measurement noise could possibly obscure a factor of 2 difference.
- 6) Sulfate Formation: Good sulfate data were not obtained far downwind when Unit 7 was not operating so that sulfate formation in the plumes from the scrubbed and unscrubbed units could not be directly compared. The aerosol data imply that sulfate formation rates in the scrubbed and unscrubbed plumes are similar.
- 7) Primary Sulfuric Acid: The scrubber on Unit 8 removes nearly all of the primary sulfuric acid. Estimated sulfuric acid stack concentrations are 8 ppm for Unit 7 and 1.1 ppm for Unit 8.

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Aerosol and Sulfate Formation in the Mixed Plumes

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- 1) Aerosol Formation Rates: The maximum aerosol formation rate was measured far downwind (40 km or more) when the plume was dilute and sunlight was strong.
- 2) Maximum Rates: When expressed as a pseudo first-order sulfur conversion rate, average aerosol formation rates as high as 2.5 percent per hour were typical between 10 a.m. and 5:30 p.m., CDT. Instantaneous rates averaged over the plume cross section could be a factor of 2 higher.
- 3) Nuclei Mode Particles: The concentration of nuclei mode particles was typically two to five times higher in the plume than the background during moderate to strong sunlight. Primary aerosol always had a large nuclei mode concentration.
- 4) Start of Photochemical Aerosol Formation: Aerosol formation was normally seen as close as 8 or 9 km (about 0.6 hours travel time) downwind, and as early as 9:15 a.m.
- 5) Sulfate Formation Rates: Between 10 a.m. and 5 p.m. measured average conversion rates from SO₂ to sulfate were between 1 and 3 percent per hour.
- 6) Sulfate Formation Levels: Day-to-day variations in ambient sulfate levels for this particular region were at least as great as the increase in sulfate levels in the sampled plumes.
- 7) Comparison of Sulfate and Aerosol Concentrations: The aerosol concentrations predicted from the plume excess sulfate measurements (using the assumption that the sulfate aerosol was a saturated solution of ammonium sulfate) were typically about 3 times higher than the measured plume excess aerosol concentrations. This large disagreement probably has more than one cause.
- 8) Nitrate Formation: No useful nitrate data were obtained because the amount of nitrate collected on the filters was near the blank values.

Primary Aerosol

- 1) Composition: Most of the primary fine particle aerosol from Unit 8 was probably sulfuric acid. Nearly all the primary fine particle aerosol from Units 1-6 and 7 was sulfuric acid.
- 2) Indications of Primary Sulfuric Acid Aerosol: Both the total amount of primary fine particle aerosol and the shape of its size distribution indicated the presence of aerosol other than fly ash.

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Gas Chemistry

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- 1) Ozone Bulges: Ozone bulges in the plume of 20 to 40 ppb were seen at 50 to 70 km whenever the plume was sampled at these distances in the afternoon. Smaller bulges were seen nearer the source and between 1030 and 1200 CDT. Increased ozone caused high NO₂/NO ratios.
- 2) NO_x Removal: NO_x was much more rapidly removed from the plume than SO₂. Afternoon removal rates may be as high as 25 percent per hour.

RECOMMENDATIONS

Future Work

- 1) NO_x Conversion: The rapid loss of NO_x in the plume should be further studied. Nitrate formation may make an important contribution to visibility degradation and acid rain. The conversion rates and products of NO_x reactions need to be better determined.
- 2) Source Separation: Scrubbed and unscrubbed sources should be separated by at least 15 km so that their plumes can be studied separately.
- 3) Instrumentation: An instrument which can accurately size particles between 0.1 and 2.0 microns should be included. Accurate data in this range would allow good estimations of the contribution of gas and liquid phase reactions to aerosol formation and give more accurate aerosol formation rates.

Further Analysis of SCRUB Data

- 1) Difference Between Sulfate and Aerosol Measurements: The large difference between the sulfate and aerosol measurements should be resolved. One way this can be done is to compare the bscat measurements with the sulfate and aerosol data.
- 2) Near Source Aerosol Formation Rates: Aerosol formation between 9 and 40 km from the source may be computed from the changes in nuclei mode particle concentrations. The amount of aerosol formed was usually too small to be detected when included in the total aerosol volume as was done for this report.
- 3) EAA Data Inversion: The EAA data should be better corrected for altitude and channel cross-sensitivity using the methods of Twomey (1975) and Ogren (1981). This may improve the agreement between sulfate and aerosol data and will improve the estimates of the aerosol formation rates.

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- 4) Gas and Liquid Phase Reactions: The inverted EAA data may be analyzed to give the contributions of gas and liquid phase chemical reactions to aerosol formation using the methods of McMurry et al. (1980). The relative importance of these processes is not well determined in areas of moderate to high humidity.

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SECTION 3

INSTRUMENTATION, DATA COLLECTION METHODS, AND FLIGHTS

THE WIDOWS CREEK STEAM PLANT

The Tennessee Valley Authority's (TVA) Widows Creek Steam Plant near Stevenson, Alabama, was studied in the SCRUB project. The plant has six 135 MW units (Units 1-6) connected to a single 305 m stack. Two additional 557 MW units have separate 152 m stacks and electrostatic precipitators with design efficiency of 90 percent. Unit 8 is equipped with a combined venturi and limestone wet scrubber, with a design efficiency of 80 percent SO₂ removal. The overall particulate removal efficiency for Unit 8 is 99.5 percent by weight. Units 1-6 have electrostatic precipitators with design efficiencies of greater than 99.5 percent. Ammonia (about 10 ppm) is added to Unit 7's flue gas to increase collection efficiency. Units 1-6 burn 1 percent sulfur coal, while Units 7 and 8 burn 4 percent sulfur coal. A diagram of this information appears in Figure 1 on page 3.

DATA COLLECTION: INSTRUMENTATION AND METHODOLOGY

The aircraft used in this study was the MRI Beechcraft Queen Air, and was instrumented to measure atmospheric trace gases, aerosol, and meteorological parameters. A list of the instruments aboard the Queen Air is in Table 1. Location of some of the instruments on the aircraft is shown in Figure 2.

Data from all continuous instruments, as well as time and event codes, were recorded on 9-track tape in digital form. These tapes were then processed at MRI and the appropriate calibration factors were applied to the data. Altitude corrections were made to correct for changes in the zero and span response of the instruments as a function of altitude.

Three types of flight maneuvers were used in this study: traverses, spirals, and orbits. Traverses gave the horizontal distribution of the measured parameters, and spirals their vertical distribution. Generally, traverses were done perpendicular to the axis of the plume, at various altitudes and distances downwind. In this way, the three-dimensional structure of the plume could be determined when the plume did not change radically during the period of the sampling. The spirals upwind of the plant gave background concentrations and the structure of the mixing layer. Orbits were done to get filter or impactor samples at a specific location.

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TABLE 1. QUEEN AIR INSTRUMENTATION

Parameter	Sampler Manufacturer and Model	Analysis Technique	Normal Measure- ment Ranges (Full Scale)	Time Response (to 90%)	Approximate Resolution
SO ₂	Meloy 285	Flame Photometric	50, 100 ppb	30 s	1 ppb
NO/NO _x *	Monitor Labs 8440	Chemiluminescence	200, 500 ppb	5-10 s	< 10 ppb
O ₃	CSI	Chemiluminescence	200 ppb	5 s	5 ppb
Sulfate	MRI Two-Mass	Flash vaporization/ flame photometric	> 3 and < 3 μm dia		~ 1 μg m ⁻³
"	ERT RSP Sampler	Ion Chromatograph	< 3 μm dia		~ 1 μg m ⁻³
Light Scattering Coefficient	MRI 1550	Integrating Nephelometer	10 ⁻⁸ m ⁻¹	1 s	0.1 x 10 ⁻⁴ m ⁻¹
"	MRI 1569	"	10 ⁻⁴ and 10 ⁻³ m ⁻¹ (Dual Range)	< 1 s	10 ⁻⁶ m ⁻¹
Condensa- tion Nuclei	Environment One Rich 100	Light Attenuation	10 ⁶ cm ⁻³	3 s	10 ³ cm ⁻³
Turbulence	MRI 1120	Pressure Fluctuations	0-10 cm ² s ⁻¹	3 s (to 60%)	0.1 cm ² s ⁻¹
Temperature	YSI/MRI	Bead Thermistor/ Vortex Housing	-50° to +50° C	5 s	0.5° C

* Not installed while the Meloy 285 Particulate Sulfur Monitor was in use.

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TABLE 1 (continued)

Parameter	Sampler Manufacturer and Model	Analysis Technique	Normal Measure- ment Ranges (Full Scale)	Time Response (to 90%)	Approximate Resolution
Dew Point	Cambridge Systems 137	Cooled Mirror	-50° to +50° C	0.5 s/°C	0.5° C
Altitude	Valdine	Absolute Pressure Transducer	0-3000 m mal	1 s	6 m
Indicated Airspeed	Valdine	Differential Pressure Transducer	23-68 m s ⁻¹	1 s	0.1 ms ⁻¹
Position	King KX170B/ HTI DVOR	Aircraft DME/VOR	0 to 359° and 0 to 150 km from the station	1 s	1° (bearing), 0.2 km (dis- tance)
Data Logger (includes time)	MRI Data System	9-Track Tape - 6 hour capacity in con- tinuous operation	0 to ±9.99 V DC		0.01 VDC
Stripchart Recorder	Linear Instruments	Dual channel	0.01, 0.1, 1, 10 VDC	< 1 s	
Aerosol Charge Acceptance	Washington University	Aerosol Charge Acceptance	~ .01-.1 μ particles	~ 1 s	
Particulate Sulfur*	Meloy 285	Upstream SO ₂ Scrubber/Measure- ment of total sulfur	66 μg S m ⁻³	30 s	Relative changes in particulate sul- fur only

* Not installed while the Monitor Labs 8440 NO/NO_x Monitor was in use.

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TABLE 1 (continued)

AEROSOL SIZE DISTRIBUTION MEASUREMENTS		
Instrument	Size Range	Method
TSI 3030*	.0056 - 1 μm	Aerosol Charger/Mobility Analysis
Royco 218/MCA*	.56 - 18 μm	Optical Particle Counter with Multichannel Analyzer
Knollenberg ASSP	3 - 45 μm	Axial Scattering Spectrometer Probe
Lundgren Impactor (modified by the University of Calif. at Davis)	10 to < 1/2 μm	4 stage impactor with final filter. Diameters of 50% cutoff: 4, 2, 1, and 0.5 μm .

* Automatic bag sampling system for TSI 3030 and Royco 218; bagfill requires about 4 seconds

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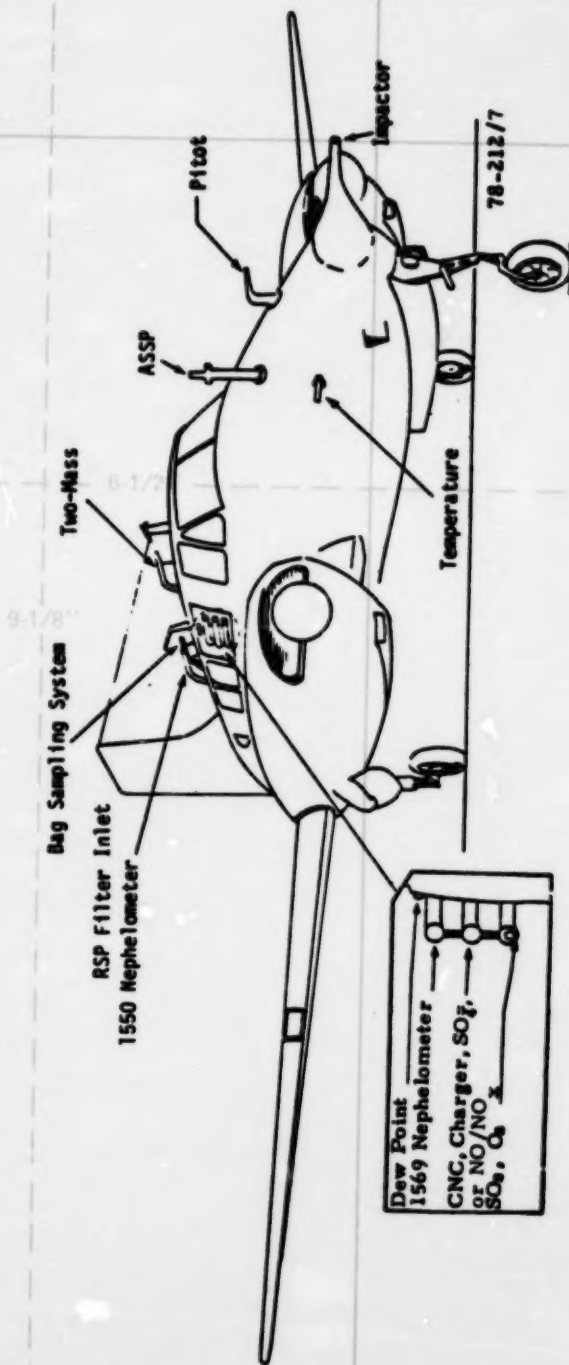
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78-212/7

Figure 2. MRI Queen Air sample inlet lines and external probes.

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Ground reference points were used for the endpoints of each traverse, and the location of each spiral.

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To produce cross sections, the data from the traverses were plotted in vertical or horizontal cross sections, with the endpoints of each traverse fixing the traverse line. Contours were then drawn. Since the data for one cross section require ~15-60 minutes to collect, these cross sections give the true plume cross sections only for steady state plumes.

Particulate sulfur (sulfate) concentrations were measured by flash volatilization and flame photometric analysis of Two-Mass filters (Husar et. al., 1976) and by ion chromatography analysis of the RSP filters. The filter material for the Two-Mass samples was glass fiber; the RSP filters were Teflon coated glass. When activated, the filter samplers sampled continuously from the ports outside the aircraft shown in Figure 2. The flow rates were about 50 and 25 l/min for the RSP and Two-Mass samplers, respectively. All sample volumes were reduced to standard conditions of 25° C and 1013.2 mbar. Both samplers have a particle size cutoff of about 3 μ m.

RSP filters were also analyzed for nitrate by ion chromatography. These results were not useful since the nitrate levels on the filters were near the values found on blank filters.

Elemental analyses of the Lundgren impactor samples were also conducted using Particle Induced X-Ray Emission (PIXE). Some of these results are in the SCRUB data volume (Stith, et al., 1979a); additional results are available upon request to MRI.

SUMMARY OF SAMPLING PROGRAM

A total of ten flights were conducted by MRI at the Widows Creek site during August 17-25, 1978. A short summary of the flights made by MRI is given in Table 2. The data collected by MRI are available in a Data Volume (Stith et al., 1979a) and on magnetic tape.

Other groups have participated in the SCRUB program. TVA sampled trace gases and particles using an instrumented helicopter. The University of Minnesota did similar sampling from an instrumented van. TVA also provided plant operation and meteorological data. Midwest Research, Inc. measured emissions of the scrubbed unit.

Several of the flights conducted by MRI provided studies of the scrubbed and unscrubbed plumes. On August 17 and 23, morning and afternoon flights were made. On these days, Unit 7 (the largest unscrubbed unit) was not operating. These days give data on scrubbed and mixed plumes. On August 19, morning and afternoon flights were made while all the units were operating.

In the following chapters, results of the analysis of the flight data are given.

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TABLE 2. SCRUB PROGRAM SUMMARY

Cart #/ Date	Flight Objective	Sampling Period (CDT)	Plume Sampling Distances (km)	No. of Traverses/ Spirals/ Orbits*	No. of Samples			Comments
					RSP	Impactor	Two-Mass	
29/ 17 Aug	Characterization of unit #8 (scrubbed) plume	0845-1224	0.5, 3, 9 downwind	0/2/16	3	5	8	Unit #7 not operating
30/ 17 Aug	Duplication of AM sampling for AM/ PM comparison	1551-1913	0.5, 2, 7	0/2/15	4	5	7	Unit #7 not operating
31/ 19 Aug	Long range plume characterization	0630-1108	0.5, 9, 20, 45, 75	10/3/10	6	5	13	Good plume characterization; Pre- cipitators out of service.
32/ 19 Aug	Continuation of AM flight	1407-1741	1, 9, 13, 17, 25, 30	8/3/7	2	2	10	Vertical structure determination at ~25 km downwind; near source char- acterization; plume spread out and patchy beyond 10 km; Precipitators out of service.
33/ 21 Aug	NO _x plume chem- istry determina- tion; comparison flights with TVA helicopter	0647-1031	15-20, 30	14/2/1	3	3	7	Plume spread out and shifting - poor characterization data
34/ 22 Aug	Sunrise experi- ment on unit #8 plume	0609-0835	0.5, 10	6/2/10	1	1	4	Experiment terminated due to low clouds and fog; limited sampling within 10 km of plant; poor plume definition - shifting winds
35/ 23 Aug	Long range plume characterization flight; sampling in conjunction with TVA	0915-1322	15, 50	13/2/2	5	5	6	Good plume characterization data; documentation of NO, NO _x and O ₃ chemistry; documentation of plume O ₃ bulge; unit #7 not operating

*Circles around the stacks are included as orbits.

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TABLE 2 (continued)

Cart #/ Date	Flight Objective	Sampling Period (CDT)	Plume Sampling Distances (km)	No. of Traverses/ Spirals/ Orbits*	No. of Samples			Comments
					RSP	Impactor	Two-Mass	
36/ 23 Aug	Continuation of AM sampling; sampling in con- junction with TVA	1441-1907	13, 50, 70	7/1/5	1	1	13	Unit #7 not operating
37/ 25 Aug	Sunrise study - document history of plume and background be- fore, during, and after sunrise	0511-0936	1, 8, 20	2/2/19	0	7	8	Sun first visible 0620; close in plume samples were of the plumes from units #7 and #8
38/ 25 Aug	Continuation of AM flight	1030-1316	43-50, 70	6/1/4	0	4	4	Good (light) plume definition at 48 km not found at 70 km

*Circles around the stack are included as orbits.

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SECTION 4

DAILY WEATHER AND FLIGHT SUMMARY

This section summarizes the weather and flight conditions for each day of the SCRUB study. A detailed description is in the TVA Data Supplement (Meagher et al., 1978b).

The weather varied little during most of the study days. The days were mostly clear and the plume was well mixed by 10 or 11 a.m. each day. A moderate to strong radiation inversion formed each night and broke up by about 8 or 9 a.m. Fog occurred on mornings of the 17th, 22nd and 25th. Winds were usually moderate at plume elevation, typically 10-15 km/hr.

August 22 was an exception to the above pattern. A low stratus overcast persisted until about noon. Little sampling was done on this day.

AUGUST 17

9-1/8"

On August 17, 1978, morning and afternoon flights were conducted while the largest unscrubbed unit (#7) was not operating. At 0.5 km downwind, sampling was in the scrubbed plume.

The weather was characterized by warm humid flow over the area accompanied by afternoon and evening convective activity. A radiation inversion in the early morning hours broke up about 0930 CDT. Ground fog was present earlier. The afternoon was unstable with light precipitation from late afternoon thundershowers. Winds during the morning near plume elevation were from 7-22 km/hr from the west-southwest. The wind died down during the afternoon.

Aircraft sampling was conducted near the plant by flying circles around the stacks and penetrating the plume at about 0.5 km downwind. In-plume orbits were then done at a near 3 km and 9 km during the morning and 7 km during the afternoon flight. Shallow background spirals covering the plume vertical extent were done to get background air data.

The plume from the tall stack (Units 1-6, unscrubbed) was seen above the aircraft during the passes at 0.5 km. At the greater distances, the tall stack plume was mixed with the lower plume.

The plume during the morning flight was relatively well defined; however, during the afternoon the plume was more spread out.

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During the period 0500-2400 (CDT), Unit 8 (scrubbed) was operating at a relatively steady level with hourly gross generation between 275 and 320 MW.

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AUGUST 19

On August 19, 1978, morning and afternoon flights were conducted while all units were operating. However, only about half the precipitators on Units 1-6 were functioning, and the precipitator on Unit 7 was shut down.

A maritime tropical air mass was over the area and associated with a subtropical high pressure system over the southeastern United States. A radiation inversion developed to about 650 meters altitude during the morning hours, with final breakup occurring by about 1000 CDT. Winds at plume elevation were between 7-14 km/hr out of the northwest during the morning. Wind speed was slightly higher during the afternoon and was out of the southwest. No precipitation occurred.

During the morning flight, 0630-1108, aircraft sampling near the plant was conducted by flying circles around the stack and penetrating the plume at about 0.5 km downwind. The aircraft then moved out to successively greater distances downwind, and made traverses through the plume and orbits in the plume. The plume was followed out to a distance of about 75 km. Mixing heights were about 1100, greater than 1500, and 1200 meters at 0930, 1540, and 1640, respectively.

During the afternoon, another long-range characterization flight was attempted. However, the wind had shifted, and the plume was much more broken up and hard to follow. Consequently, the sampling which was done was rather limited. Most EAA data in the afternoon was flawed and was not analyzed.

AUGUST 21

On August 21, a morning flight was made and all units were operating. The plume was spread out and shifting so that sampling was limited.

A modified maritime polar high-pressure area dominated the southeastern U. S. A subsidence inversion persisted at 1400 meters throughout the day. Lower inversions, at 580 and 1050 meters, dissipated by 10 a.m. CDT. Winds were about 15 km/hr during sampling but unsteady in direction.

Orbits and traverses were flown between 15 and 30 km.

AUGUST 22

On August 22, sunrise measurements were planned but were postponed due to overcast and fog. Sampling was limited to within 10 km of the plant. Data on this day were only analyzed for primary sulfuric acid aerosol at 0.5 km. Both Units 7 and 8 were operating.

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AUGUST 23

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On August 23, the unscrubbed unit (#7) was not operating so that sampling was done in either the scrubbed plume or the mixed plume from Units 1-6 and 8. Morning and afternoon flights were made.

The background air was quite polluted with levels of b_{sp} between 2.5×10^{-4} to $3.5 \times 10^{-4} m^{-1}$. The radiation inversion which had formed by early morning to about 800 meters had broken up entirely by about 0930. Winds at plume elevation were rather strong ($\sim 6-7 m s^{-1}$) during the early morning hours, but by 1000 had died down to about $3 m s^{-1}$ from the southerly direction where they remained for the rest of the sampling period. Scattered to broken clouds were in the area, with bases at about 1700 m; no precipitation occurred.

During the morning flight, traverses were made at 11 to 14 km and at 50 km downwind of the plant. A spiral through the plume and a background orbit were also done. During the afternoon flight, traverses and orbits were made at 70 km downwind, and these were repeated at 50 and 13 km downwind. Mixing heights were above 2000 and 3000 meters at 1 p.m. and 4 p.m., respectively.

During these measurements, the scrubbed unit (#8) was operating at a steady level (235-245 MW, hourly gross generation). Units 1-6 (tall stack, unscrubbed) were generating about 775 MW.

AUGUST 25

On August 25, early morning and late morning flights were made. All units were operating. The purpose of the early morning flight (Sunrise Experiment) was to document the effect of sunlight on aerosol formation. Morning flights were at 0.5, 3, 8 and 20 km downwind. Afternoon flights were at 45 and 70 km.

A large high pressure system covered the southeastern United States. The radiation inversion began breaking up at about 8 a.m. The atmosphere was unstable during the day with thunderstorms in the evening. The atmosphere was mixed to about 1500 meters by 11 a.m. Winds at plume elevation were about 8 and 15 km/hr from the west during the morning and afternoon flights, respectively.

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SECTION 5

PHOTOCHEMICAL AEROSOL FORMATION IN THE WIDOWS CREEK PLUME

Photochemical aerosol formation in the Widows Creek plume was calculated in two ways:

- 1) From the sulfate concentrations determined from the filter samples.
- 2) From the aerosol size distributions measured with the EAA and bag sampling system.

For both methods, the difference between the plume and background concentrations gives the formation in the plume. Sulfate is a major product of photochemical reactions and condenses along with water (depending on the humidity) and many of the other photochemical products to form the submicron aerosol measured with the Electrical Aerosol Analyzer (EAA).

The sulfate measurements are discussed in the next subsection. The EAA results follow the sulfate subsection. The results from the two methods are compared in the final subsection.

Sulfate was measured on three types of filter samples collected in the Queen Air: a modified Lundgren impactor, MRI Two-Mass, and ERT RSP samplers. The sulfate concentrations given by these methods are compared and discussed and then conversion rates of SO_2 into sulfate are presented and discussed.

SULFATE MEASUREMENTS

Sulfate in the impactor samples was measured as (total) sulfur by Particle Induced X-Ray Emission (PIXE). The sulfur on the impactor filter and last stage were added together so that total sulfur in particles less than about 1 micron is reported. Most sulfur was on the filter and last stage. We checked the data for anomalous sulfur from larger particles blown off the upper stages and found this error to be unimportant. The sulfate on the Two-Mass filter was measured by fly ash volatilization followed by flame photometric analysis (FPD) (Husar, et al., 1976). The sulfate on the Teflon coated glass fiber RSP filters was extracted with water and measured by ion chromatography (IC).

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Of the three methods, we judge the IC analysis of the RSP filters to be the most accurate because it is the simplest and least likely to introduce bias into the data.

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Correlation of PIXE and Ion Chromatography Results

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Figure 3 shows a plot of PIXE versus IC results. The IC sulfate concentrations have been converted to sulfur per cubic meter so that they are directly comparable to the PIXE results.

The data have considerable scatter, which is typical for the PIXE analysis of very lightly-loaded filters. Three points, shown with squares, are outliers and were not used in further analysis. (The two squares on the X-axis had sulfur below the PIXE detection limit.) The correlation coefficient square (r^2) for all the remaining points is 0.26 and is too small, in our judgment, to draw useful inferences on the relation between the IC and PIXE results.

However, in Figure 3 the points appear to be grouped into a set which is rather well-correlated, the dots, and a second uncorrelated group, the circled dots. r^2 for these groups is 0.80 and 0.03, respectively.

If the circled dots are caused by an error source which was not present in all data, then significance can be given to the better correlated points.

Correlation of Fly Ash Volatilization - FPD and Ion Chromatography Results

Figure 4 compares the FPD and IC sulfur results. Again the IC sulfate has been converted to μg sulfur/ m^3 . The correlation is quite good and r^2 is 0.74. Unlike the PIXE comparison, the points appear uniformly scattered about a regression line. The finding that the FPD method gives lower ambient concentrations than the IC method is consistent with results from other studies. Identical results were obtained in the 1978 VISTTA study (Zwicker et al., 1981) using the same aircraft measurement system. Also, the FPD results were 0.38 times as large as the mean of all results in the EPA sponsored comparison of sulfate measurement methods conducted in Charleston, West Virginia (Camp, 1980).

Discussion of Sulfate Data and Use in Further Analysis

We used only FPD data in further analysis since it was well-correlated with the IC results, and many more FPD than IC points were available. We did not use the PIXE data because of its uncertain correlation with the IC data.

Because sulfate measurement method intercomparisons have shown IC data to be more accurate than FPD data (Camp, 1980), we corrected the FPD data based on the regression with the FPD results as the independent variable shown in Figure 4. Since a background air sulfur measurement was always subtracted from plume measurement, only the slope of the correlation is important. The two lines in Figure 4 correspond to the two choices of independent variables and are both reasonable fits to the data. The slopes for the IC and FPD results as the independent variable, but plotted with the IC results on the X-axis are 0.52 and 0.70, respectively. We multiplied all FPD concentrations by $1/0.70$ or 1.43 since we want to approximate IC results from the

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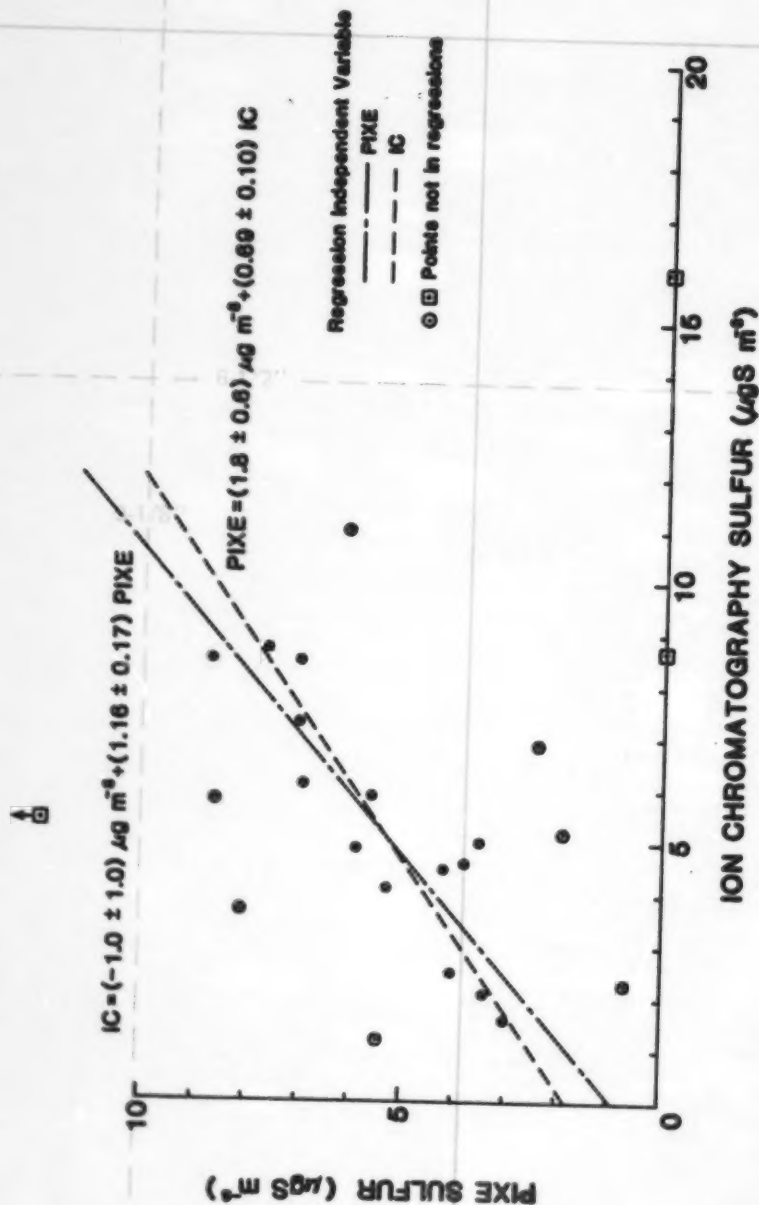


Figure 3. Comparison of sulfur concentrations from ion chromatographic analysis of RSP filters and Particle Induced X-Ray Emission (PIXE) analysis of Lundgren Impactor samples.

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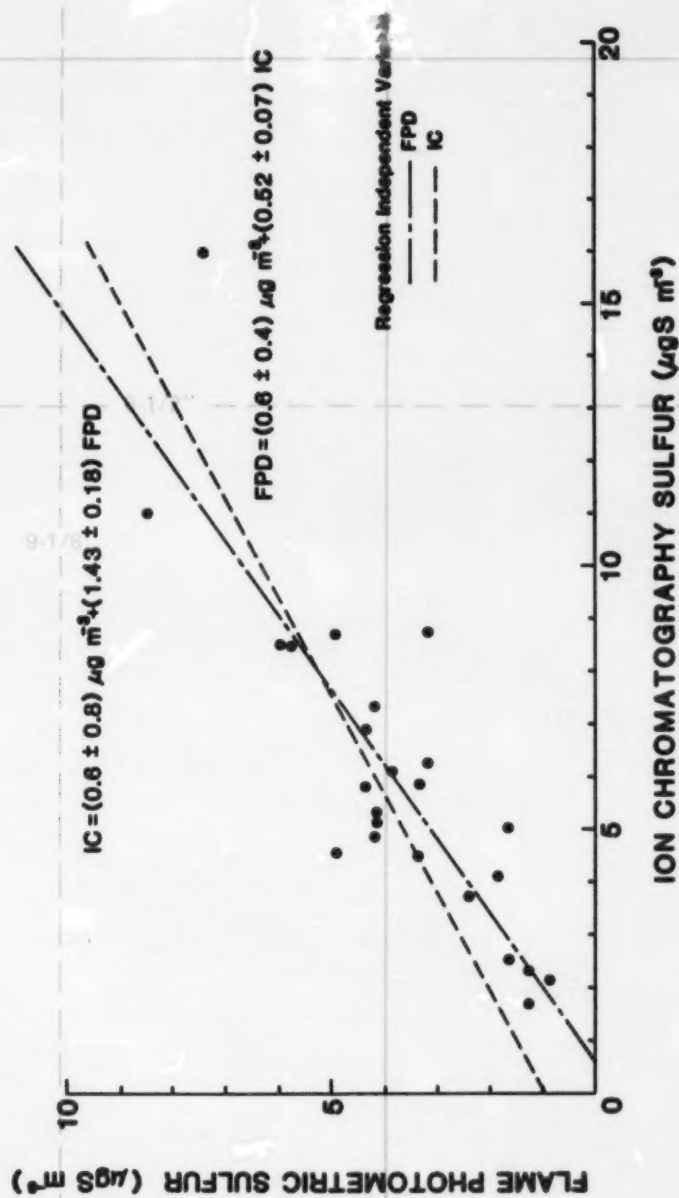


Figure 4. Comparison of sulfur concentrations from ion chromatographic analysis of RSP filters and flash volatilization/flame photometric analysis of Two-Mass filters.

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FPD data (i.e., FPD is the independent variable). This correction factor for FPD data is much smaller than the one reported by Camp (1980).

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SULFATE FORMATION RATES

Table 3 shows the sulfate formation rates in the Widows Creek plume obtained from the FPD data corrected by the IC data. The third column from the right shows the ratio of sulfur present in sulfate to the sulfur present in SO_2 . The two right-most columns give the sulfur conversion rate per hour averaged over the entire travel time and the rate between downwind distances when the data were taken in approximately the same air parcel. Averages of data are shown where appropriate.

Several patterns are apparent in the data:

- 1) Some primary sulfate is present. The fraction, but not the total, is probably higher in the Unit 8 plume.
- 2) Sulfur is converted to sulfate as the plume travels downwind. (The ratio of sulfate to SO_2 increases with time.)
- 3) The conversion rate increases with downwind distances.
- 4) The conversion rate is slow or zero near the source and at times when sunlight is not strong.
- 5) The data have considerable scatter and some are obviously bad.

These items will be further discussed after the following subsection.

Sulfate Formation - Data Reduction

The ratio of particle to gas sulfur ($\text{S in SO}_4/\text{S in SO}_2$) in Table 3 was calculated from the Two Mass samples analyzed by FPD and corrected as described above. Sulfur conversion rates were calculated by a procedure similar to the one used by Husar et al. (1978): the conversion rate is the change in the fraction of sulfur present as sulfate per unit plume travel time. This method will overestimate the conversion rate if much SO_2 is deposited on the ground before the measurements are made or if the total conversion is large (which it was not). Most of the plumes sampled in this study were either above the terrain entirely or had the main portion of the plume above the terrain. Consequently, little SO_2 should have been lost by dry deposition. The sulfate formed in the plume was calculated by subtracting the sulfate concentration in the background air near the plume from that measured in the plume.

Plume travel times were determined from the average wind speed at plume elevation during the time aloft and are probably accurate to about 20 percent. Wind speeds were from pibal measurements made by TVA.

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Pairs of high and low values were excluded from average data in Table 3 if scatter was excessive. The plus-minus signed numbers in the table are standard deviations of the averages.

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TABLE 3. IN PLUME SULFATE FORMATION BASED ON FILTER MEASUREMENTS

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Date	Sample Times	Power (MW) Units			Distance (km)	Total Travel Time (hrs)	Plume Excess (Sulfur as SO ₂) (%)	Sulfur Conversion Rate (%/hour)		Integrated Solar Flux (Ly)
		1-6	7	8				From Start	From Previous Distance	
8/17	Morning 0853-0933 1024-1116 1129-1159	500	0	320	0.5 3 9	n.a. .23 .62	1.6 0.9 1.8	n.a. n.a.		n.a. 15 45
8/17	Afternoon 1551-1635 1732-1805 1821-1852	520	0	320	0.5 3.01 7.0	n.a. .43 .84	0 1.8 14.73	n.a. n.a.		n.a. 12 13
8/17	Average 0853-1852				≤9		1.6±.2 ²	n.a.		21±8
8/19	Early Morning 0717-0736 0756-0826 0845-0944 0917-0932 0955-1007 1011-1026 1036-1053	441	305	245	0.5 9 24 25 45 47 75	n.a. 0.6 1.6 1.7 2.7 3.4 5.1	.11 .6 1.0 .7 3.7 3.6 6.5	n.a. n.a. 0.6 0.4 1.4 1.1 1.3		11 48 54 90 113 143
8/19	Average 0717-0826 0955-1053				≤9 45-75		0.4±.2 4.6±1.0	1.3±.1	1.9±.4	115±15
8/19	Afternoon 1407-1424 1516-1529 1553-1618	686	305	245	58 0.5 9-13	4.7 n.a. .56	9.9 1.5 3.8	2.1		329 31
8/21	Morning 0734-0844 0857-0925 0936-1031 0949-0959	520	295	230	15-20 30 15 20	1.4 1.7 1.2 1.6	.3 1.3 .44 -6.6 ³	0.2 .8 0.4		18 36 46 51
8/21	Average 0734-1031				15-30	1.4	.7±.3	.5±.2		38±7
8/23	Morning 0944-0950 1134-1231 1252-1259	770	0	245	11-14 50 50	.88 3.6 3.6	-15 ³ -1.2 ³ 28 ³			39 178 209
8/23	Afternoon 1441-1531 1710-1719 1822-1828	780	0	245	70 50 13	6.5 4.8 1.4	4.33 2733.4 1113.4	.7		379 256 24
8/25	Morning 0543-0645 0652-0736 0830-0845 0857-0912	750	255	285	0.5 0.5 20 8	0.06 0.06 .87 .52	.4 1.3 -1.7 -1.0	n.a. n.a.		0 0 20 16
8/25	Average 0543-0912						0.0±.5			9±5
8/25	Late Morning 1053-1108 1240-1255 1301-1316	760	290	255	45 50 45	3.5 2.8 2.8	2.2 8.1 8.8	.6 2.9 3.2		139 189 193
8/25	Average 1240-1316				47.5	2.8	8.4±.3	3.0±.2		191±2

- 1) May be left over plume, travel time very uncertain.
2) High and low values not included in average.
3) Number unreliable.
4) SO₂ concentration average during pass less than 2.3 ppb.
n.a. - not applicable

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Primary Sulfate

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Nearly all measurements less than 10 km downwind show more sulfate in the plume than in the background, particularly the averaged data for 8/17 and 8/19. An exception is the data on the morning of 8/25 which indicate zero primary sulfate. However, the scatter in these data is large enough so that the results on 8/17 and 8/19 are within the standard deviations shown. The reverse is not true: zero primary sulfate does not lie within one standard deviation of the 8/17 and 8/19 averages. The primary sulfate most probably results from the sulfuric acid in the flue gas. The ratio of primary sulfate to SO₂ in Unit 8 (8/17) is higher than when Unit 7 and 8 were operating. This suggests that SO₂ was being removed more efficiently by the scrubber in Unit 8 than the sulfuric acid; however, the scatter in these data make this conclusion somewhat uncertain. The total amount of sulfate seen while Unit 7 was operating was higher, however. Primary sulfate was also indicated by the EAA measurements.

Sulfate Conversion Rates

—The data in Table 3 show that sulfate, as a percentage of sulfur present, increases with time. This indicates conversion of SO₂ to sulfate. Although the data have considerable scatter and the data on 8/23 are bad, the balance of the data is good enough to indicate that the conversion rate increases as the plume moves downwind. This effect is likely due to plume dilution and increasing sunlight. Most of the measurements at the farther distances were made later in the day than the closer measurements. The increase in conversion rate is also indicated by higher rates between two downwind distances than the corresponding average over the total travel time.

Some in plume conversion beyond the primary sulfate is suggested at intermediate distances, particularly on the morning of 8/19. However, we judge the data too noisy to make a firm conclusion. The data point at 9 to 13 km on the afternoon of 8/19 seems too high to be believable.

At times when sunlight intensity is low, e.g. early in the morning, the data show no indication of in plume sulfate formation beyond the primary sulfate.

Scatter and Bad Data in the Sulfate Measurements

The data set in Table 3 has several excessively large sulfate numbers and several negative sulfate numbers. Negative sulfate formation is physically unrealistic; however, some small negative numbers are expected from measurement noise when sulfate formation is small. The sulfate numbers at 13 and 50 km on the afternoon of 8/23 are probably inflated because of the small average SO₂ concentration, which was less than 2.3 ppb. A few ppb error in the SO₂ may be the problem instead of the sulfate analysis. However, all the data for 8/23 appear suspect: the numbers are either too large or too small.

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As a whole, the data appear to be reasonable; however, the quantity of unexplained suspect data is large enough to indicate that some caution should

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be used in asserting conclusions based on this data set alone. The apparent trends in the data are generally consistent with the results from other studies (Gillani et al., 1981).

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AEROSOL FORMATION

Aerosol formation in the Widows Creek plume was maximized by plume dilution and noon-day sunlight. Aerosol formation rates were calculated from aerosol size distributions measured with the EAA and its bag sampling system. These distributions included particle sizes from about 0.0056 to 1.0 micron in diameter and, thus, included the size range in which photochemical aerosol formation occurs. Data above 1.0 microns were excluded from analysis because growth from photochemical reactions was not expected to be significant in this size range.

Data Reduction

The EAA system produced about one size distribution about every five minutes. These distributions were nearly point measurements since the EAA sampled from a bag which was filled with outside air in about 2.5 seconds.

The EAA data were screened to eliminate obviously bad results and then were grouped by flight and position downwind from the source. At each position the best data were averaged. Typically two or three background distributions were averaged to get an average background distribution, and two to five distributions from different points or passes through the plume at approximately the same altitude and downwind distance were averaged to get an average plume distribution. If enough data were available, two or three average plume distributions were calculated. In a few cases, single distributions were used.

The individual distributions were averaged because of their considerable variation. The majority of the variation was real. The size distribution variability from point to point in the plume, and to a somewhat lesser extent in the background air, was high. Other noise sources were the sensitivity of the EAA to vibration, small changes in its air flow rates, and electrical noise. These are difficult to eliminate on aircraft.

The size distributions were calculated from the measured EAA current in each size channel by multiplying the current in them by a "calibration constant." These constants can vary with the size distribution because of the cross sensitivity between the EAA size channels. The constants used for channels 3 through 10 (0.01 to 1.0 microns) were those from Whitby and Cantrell (1979) for a bimodel lognormal distribution with peaks in the volume distribution at 0.04 and 0.35 microns and geometric standard deviations of 1.7 and 2.0, respectively. Since the distributions seen in the Widows Creek plume had peaks near those sizes, the Whitby-Cantrell constants for channels 3 through 10 are expected to be more accurate than those given by Lui and Pui (1975) which also appear in the EAA instruction manual. In most channels the Whitby-Cantrell constants are within 25 percent of Lui and Pui constants. We used the channel 2 constant (sizes 0.005 to 0.01 microns) from Lui and

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Pui since the Widows Creek size distributions often had considerable particle concentrations in this range, unlike the Whitby-Cantrell size distributions.

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When we calculated total aerosol volume or mass concentrations, we neglected the aerosol volume in EAA channel 10 for two reasons: 1) the decreased air pressure at flight altitudes and EAA cross-sensitivity caused the indicated channel 9 concentrations to be higher and channel 10 concentrations to be much higher than the correct values, and 2) channel 10 was very noisy. Neglecting channel 10 volumes approximately removed the effect of altitude on the EAA response when calculating total aerosol concentrations and eliminated considerable noise from the reduced data.

Aerosol Formation Rates

Table 4 shows plume excess aerosol and aerosol formation rates calculated from EAA data for the entire program. The table shows the distance and travel time from the source and times and formation rates between downwind distances when data were taken in approximately the same air parcel. The plume excess aerosol volume is divided by SO_2 concentration since the absolute concentrations of plume excess aerosol varied with the (large) changes in plume dilution. Normalizing the formation rates to SO_2 concentration this way cancels out the effect of dilution and allows estimation of the conversion rate of SO_2 aerosol in the entire plume.

The plume excess volumes, V_{pe} , were calculated using equation 1:

$$V_{pe} = V_p - V_B - \overline{SO_2} \left(\frac{V^*}{\overline{SO_2}^*} \right) \quad (1)$$

where V_p and $\overline{SO_2}$ are the average aerosol volume and SO_2 concentration in the plume at a given distance respectively, V_B is the average aerosol concentration in the background air near the plume, and $(V^*/\overline{SO_2}^*)$ is the ratio of primary source aerosol concentration to SO_2 concentration obtained from measurements near the source. The final term in equation 1 is the contribution of the primary plume aerosol. Because of the uncertainties in measurement of V_p , V_B , and $(V^*/\overline{SO_2}^*)$, V_{pe} may be negative. Aerosol concentration is in units of cubic microns per cm^3 . The SO_2 concentration is in parts per billion (ppb).

The rate of SO_2 conversion to aerosol is of primary interest. The SO_2 conversion rate is the normalized volume formation rate times a constant, C_s , which depends only on the aerosol composition. We assumed the aerosol to be a saturated solution of ammonium sulfate since: 1) the sulfuric acid formed from SO_2 will be mostly neutralized by the ammonia present; and 2) the relative humidities were typically 60 to 80 percent so that the ammonium sulfate would have deliquesced. Under this assumption, the aerosol is about 45 percent ammonium sulfate by weight, the specific gravity is 1.20, and C_s is 0.092. The units of C_s are ppb SO_2 equivalent per $(\mu m^3 \text{ aerosol}/cm^3)$.

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Although the exact composition of the secondary aerosol is not known, values of C_s calculated for the possible composition extremes suggest that it should be within a factor of 2 of the correct value and probably is within a factor

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TABLE 4. AEROSOL GROWTH RATE CALCULATIONS

Date	Time	Power (MW)			Distance (km)	Total Travel Time	Time from Prev. Meas.	Aerosol Growth			Percent/Hour Conversion		SO ₂ conc. ppb	Growth Rate From Start μm ³ / (hr-cm ³)
		1-6	Units					Excess Plume Vol./ SO ₂	Rate/ppb SO ₂ μm ³ /(cm ³ -ppb-h)		From Start	From Prev. Dist.		
			7	8					From Start	From Previous Distance				
8/17	Morning 1024-1115 1128-1158	500	0	320	3 9	0.23 0.62		<0 <0					36 56	
8/17	Late Afternoon 1732-1751	520	0	320	3 7	0.43 0.84		0.055* <0	0.13		1.2		22.5 32	2.9
8/19	Early Morning 0759-0825 0847-0907 0916-0926 0956-1005 1018-1023 1039-1050	441	305	245	9 24 24 45 45 75	0.6 1.6 1.7 2.7 3.4 5.1		<0 <0 <0 <0					1004 107 116 62 72 27	
8/19	Afternoon 1412-1415	686	400	230	58	4.7		0.19	0.04		0.37		15	0.60
8/21	Morning 0811-0839 0908-0921 0937-1029	520	295	230	15 30 17.5	1.0 1.7 1.4	0.7	0.000 0.016 0.050†	0.009 0.036†	0.023	0.09 0.32†	0.20	189 50 52	0.45 1.9
8/23	Morning 1024-1041 1134-1236	770	0	245	11-14 50	0.88 3.6	2.7	0.023 0.28	0.026 0.078	0.095	0.24 0.72	0.88	85 18	2.2 1.4
8/23	Afternoon 1450-1526 1714-1723 1836-1845	780	0	245	70 50 13	6.5 4.8 1.4		1.67 1.15 0.009	0.26 0.24 0.006		2.4 2.2 0.059		3.5 5.5 21	0.91 1.3 0.13
8/25	Early Morning 0544-0735 0833 0902	750	255	285	0.5 20 8	0.06 0.87 0.52	0.35	0.000 0.009 <0	0.010		0.010		634 89 75	0.89
8/25	Late Morning 1055-1106 1135-1138 1311-1314 1242-1252	760	290	250	45 45 45 50	3.5 3.5 2.8 2.8		0.078 0.131 0.26 0.84	0.022 0.037 0.093 0.30		0.20 0.34 0.85 2.8		22 31 3.5 10	0.48 1.1 0.33 3.0

*May be left over plume, travel time very uncertain.
†Poor background data (used 30 km background).

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of 1.5. Most important, the sulfate formation rate calculated from these aerosol data can be compared with that from the filter data. Since the atmospheric conditions were reasonably constant over this study, we expect the aerosol composition, and thus C_s , to be reasonably constant and not a major variable.

Table 4 shows that significant aerosol formation does not occur near the source or before about 9 a.m. even on sunny days (no cloudy days are included in Table 4). However, near or after noon and when the plume is dilute, aerosol is formed relatively rapidly. Several average conversion rates as high as about 2.5 percent/hour were seen. We think it likely that maximum (plume cross section average) rates may be about a factor of two higher since high average rates in Table 4 include times during the day where the table shows growth to be relatively slow, such as near the source or before 10 a.m. Sunlight intensity was normally at its maximum between 1200 and 1400. Maximum total conversion measured was 15 percent during the afternoon of 8/23. Figures 5 and 6 show average aerosol size distributions during periods of maximum aerosol formation.

Comparison of Aerosol Formation in Scrubbed and Unscrubbed Plumes

Although the plumes were well mixed by convection after about 10 a.m. and 10 km, the amount of SO_2 in the plumes varied considerably. About 2.5 to 3 times as much SO_2 was being released on 8/19, 8/21, and 8/25 when the unscrubbed Unit 7 was running at 290 to 400 MW compared to 8/23 when Unit 7 was down. Units 1-6 and Unit 8 boiler loads were relatively constant during all the flights. Aerosol formation rates near the greatest values observed in this study occurred both when Unit 7 was up and down. These data support the hypothesis that aerosol formation in the scrubbed and unscrubbed plumes do not differ. However, the noise in the data could obscure differences smaller than a factor of about 2.

Comparison of Nuclei and Accumulation Mode Particle Concentrations

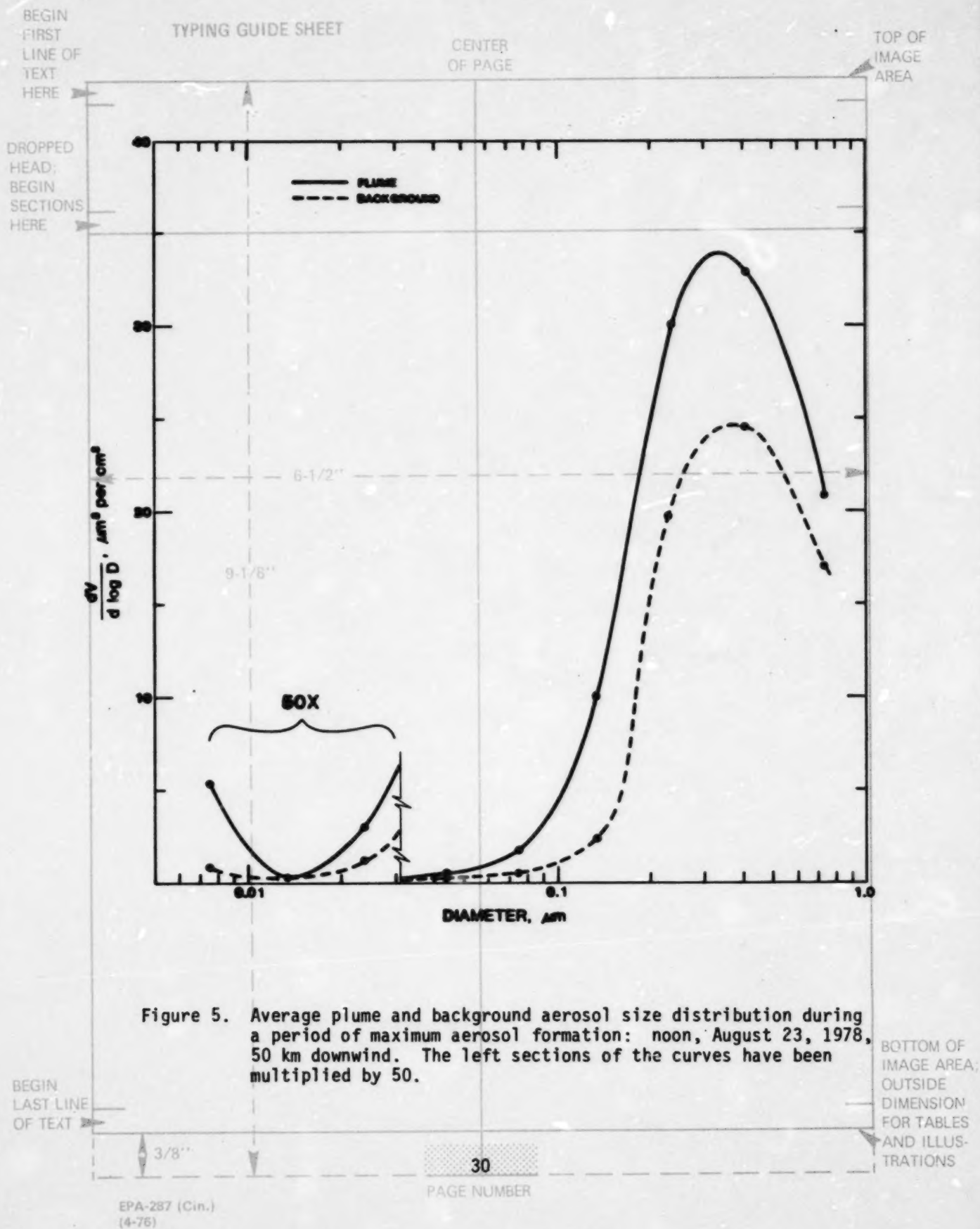
Most ambient aerosol volume (or mass) in particles less than 1 micron in diameter is in the accumulation mode, which can be approximated by a log-normal volume distribution with a peak at about 0.4 microns, and lying almost completely between 0.1 and 1.0 micron. This mode is stable and the particles in it are usually many hours old. However, when aerosol formation is rapid enough, many small particles between 0.005 and 0.1 microns form: the sum of these particles is usually called the "nuclei mode." These smaller particles coagulate rapidly with themselves and with the particles in the accumulation mode so that their lifetime is short, often only a few minutes. The presence of a nuclei mode is a sensitive indication of recent or ongoing aerosol formation because of this short lifetime and the small amount of aerosol volume needed to make detectable numbers of these very small particles.

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Table 5 shows the measured nuclei mode volumes and compares them to the accumulation mode volumes. The nuclei mode is broken into two size ranges, 0.0056 to 0.018 and 0.018 to 0.056 microns, because the nuclei mode particle distribution often did not have an obvious peak. Also, much of the material at 0.5 km downwind from 0.018 to 0.056 microns was in the tail of the larger

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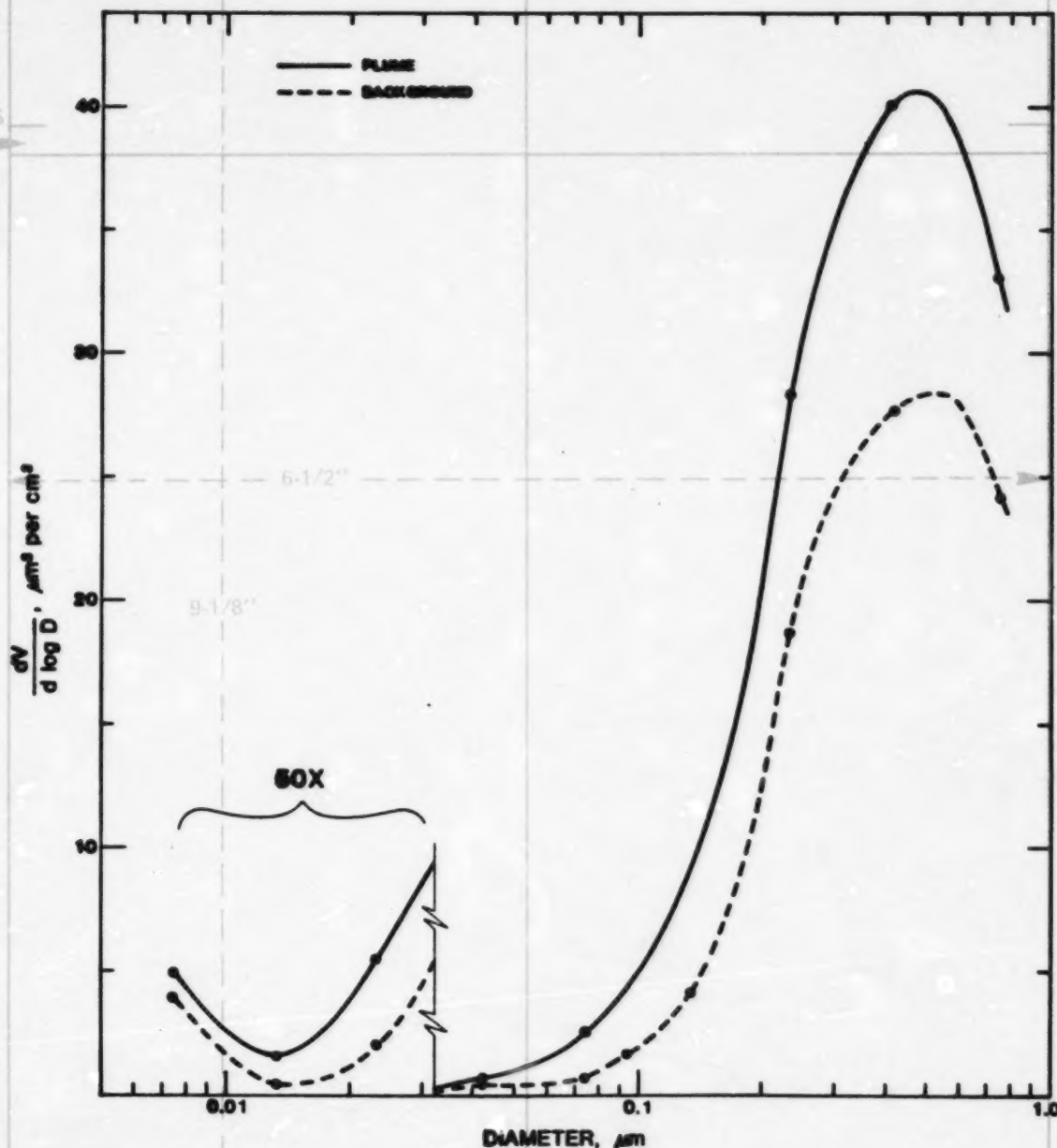


Figure 6. Average plume and background aerosol size distribution during a period of maximum aerosol formation: 1230 CST, August 25, 1978, 50 km downwind. The left sections of the curves have been multiplied by 50.

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TABLE 5. NUCLEI AND ACCUMULATION MODE VOLUME CONCENTRATIONS

Date	Time	Power (MW)			Distance (km)	Aerosol Volume ^{a,b} 0.0056 to 0.018 μ m		Aerosol Volume ^{a,b} 0.018 to 0.056 μ m		Ratio of Nuclei Mode Volume to Accumu- lation Mode Volume (%)	
		1-6	7	8		background	plume	background	plume	background	plume
8/17	Morning	500	0	320							
	0930-1005				.5	.014	.11	.061	.27	1.5	2.1
	1024-1115				3	.030	.032	.047	.12	1.6	2.5
	1128-1158				9	.008	.075	.19	.54	3.2	8.6
8/17	Late	520	0	320							
	Afternoon										
	1609-1630				.5	.018	.040	.068	.220	1.3	2.2
	1701-1751				3 ^c	.003	.023	.073	.055	1.0	0.8
	1820-1844				7	.003	.020	.048	.063	0.68	1.0
8/19	Morning	441	305	245							
	0640-0731				.5	.003	.015	.055	.92	0.6	5.0
	0800-0825				9	d	.095	d	.10	d	0.5
	0845-0907				24	0	.020	.023	.098	0.2	0.5
	0845-0926				25	0	.023	.023	.27	0.2	2.1
	0956-1005				45	d	.028	d	.12	0.2	0.8
	1018-1023				47	d	.028	d	.36	d	2.5
	1039-1050				75	d	.020	d	.045	d	0.4
8/19	Afternoon	686	400	230							
	1407-1421				58	.003	.020	.035	.053	0.5	0.6
	1521-1532				.5	.019	.023	.040	.80	1.7	12
	1558-1616				9-13	.003	.023	.043	.21	1.8	9.9
	1618-1645				17	.003	.020	.040	.10	1.7	4.2
	1658				27	d	.020	d	.11	d	1.4
8/21	Morning	520	295	230							
	0759-0839				15-20	.014	.018	.050	.32	0.7	2.2
	0911-0921				30	.002	.054	.050	.06	0.6	1.0
	0937-1029				15-20	d	.021	d	.12	d	1.1
8/23	Morning	770	0	245							
	0925-1041				11-14	.013	.028	.038	.10	0.5	0.8
	1134-1236				50	.000	.012	.065	.10	0.4	0.5
8/23	Afternoon	780	0	245							
	1450-1526				70	.003	.018	.033	.10	0.3	0.7
	1710-1752				50	0	.020	.060	.12	0.5	0.8
	1819-1845				13	.003	.020	.015	.06	0.15	0.6
8/25	Early	750	255	285							
	Morning										
	0546-0656				.5	.015	.34	.060	.61	0.5	1.6
	0713-0754				.5	.013	.06	.058	.31	0.5	1.6
	0830-0839				20	.030	.015	.030	.07	0.5	0.5
	0902-0935				8	.018	.010	.048	.24	0.4	1.8
8/25	Late	760	290	250							
	Morning										
	1045-1116				45	.018	.028	.043	.14	0.5	1.2
	1135-1138				45	d	.045	d	.27	d	1.9
	1242-1252				50	d	.025	d	.16	d	0.9
	1258-1314				45	.020	.023	.12	.12	1.1	1.2

a) Units are μm^3 aerosol/ cm^3 air.

b) Noise levels are 0.002 and $0.02 \frac{\mu\text{m}^3}{\text{cm}^3}$ for the 0.0056 to 0.018 and 0.018 to 0.056 μ m size ranges, respectively.

c) May be leftover plume.

d) No separate background data.

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primary aerosol distribution. The noise levels in the smaller and larger nuclei sizes are about 0.003 and 0.020 $\mu\text{m}^3/\text{cm}^3$.

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The striking features of Table 5 are that the nuclei mode volumes for both size ranges and the ratio of the nuclei to accumulation mode volume are almost always larger, and often much larger, in the plume than in the background. Thus, aerosol formation was nearly always indicated.

The plume nuclei mode at 0.5 km indicates that aerosol is formed soon after the plume leaves the stack since flue gas from a pulverized coal boiler has a negligible volume of aerosol less than about 0.04 microns (Markowski, 1981; Ensor, 1979, 1981, in preparation). This aerosol is very likely sulfuric acid.

Two measurements on 8/17 from 1128 to 1158 and 8/19 from 1558 to 1616 show that photochemical aerosol formation has begun within about 9 km of the source. Figure 7 shows the difference between the background plus primary aerosol and that seen in the plume on 8/17 at 9 kilometers. The number of particles less than 0.02 microns in diameter is much larger in the plume.

Significant plume excess concentrations of nuclei mode particles are nearly always seen at distances greater than 7 kilometers downwind from the source and indicate photochemical aerosol formation. Exceptions occurred in the morning before about 0830 (on 8/19 and 8/25) and after about 1700 on 8/17 and 8/23. Large nuclei mode concentrations are not expected when sunlight intensity and, thus, photochemical aerosol formation is low.

Four measurements during times when sunlight was fairly strong do not show large increases in nuclei mode particle concentrations. Three of these, on 8/19 from 1039 to 1050, and 1407 to 1421 and 8/23 from 1134 to 1226, had considerably higher aerosol concentrations than average for this study and were made where the plume was dilute. These conditions will tend to suppress nuclei particle formation because the photochemical reaction products will tend to condense or agglomerate on the larger aerosol particle and will be less likely to reach concentrations high enough to form nuclei particles. In addition, the nuclei particles which do form will be scavenged more rapidly. During the fourth measurement, on 8/25 from 1242 to 1252, both the total aerosol concentration and the background nuclei volume concentration were higher than normal so that the nuclei mode concentration in the plume was only a little greater than in the background.

The total photochemical aerosol formation rate may be computed from the changes in the aerosol size distribution for particles smaller than about 0.1 micron in diameter (Wilson, et al., 1980), as, for example, from the data in Figure 7. These calculations are sensitive to much smaller changes in aerosol volume than the methods used in the section titled "Aerosol Formation Rates", so that reliable aerosol formation rates may be calculated much closer to the source. However, these calculations were beyond the scope of this contract.

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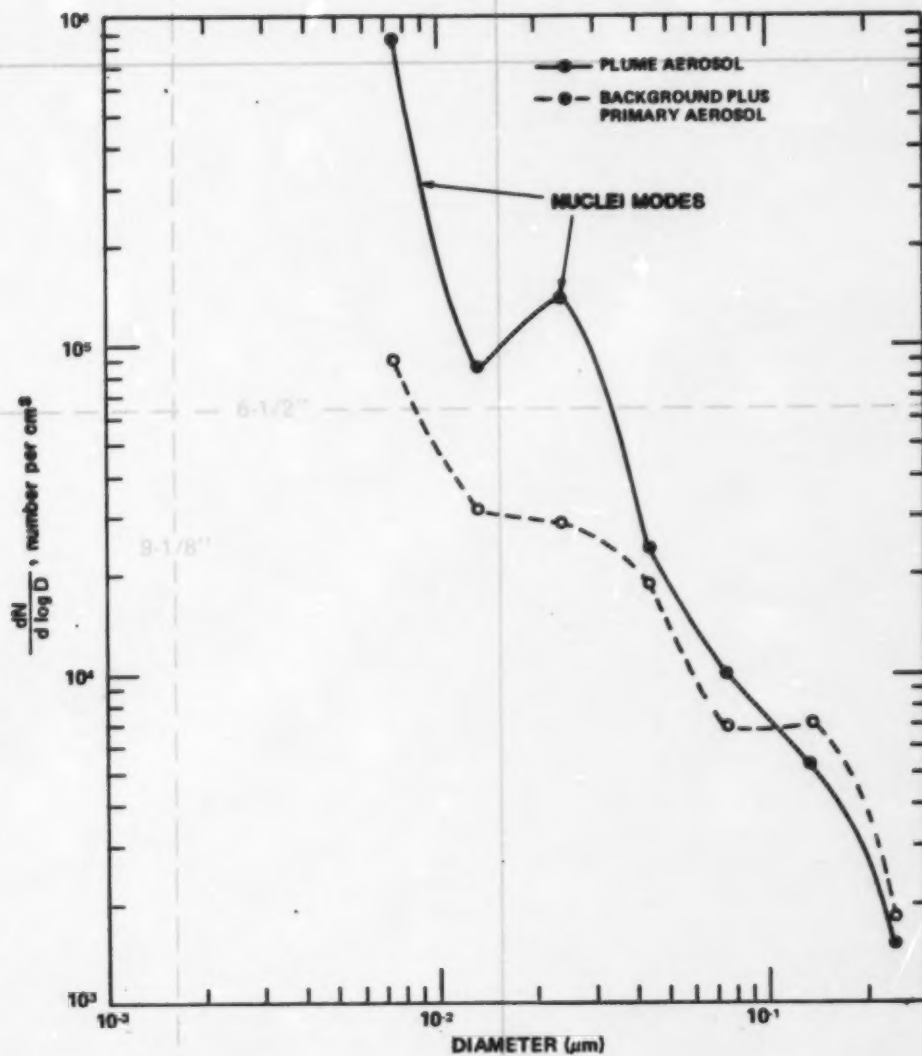


Figure 7. Plume and background plus primary aerosol distributions
9 kilometers from Widows Creek Station, August 17, 1978.

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COMPARISON OF SULFATE AND AEROSOL FORMATION RESULTS

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The sulfate and aerosol formation results are related because most of the sulfate will be in the small aerosol particles measured by the EAA. The measured sulfate concentrations can be roughly compared to the EAA data by estimating the aerosol volume concentrations they would form under conditions typical during the study.

A reasonable assumption is described in detail in the subsection "Aerosol Growth Rates", i.e., that the sulfate would form particles which are a saturated solution of ammonium sulfate. This assumption is also good for sulfuric acid since the sulfate as sulfuric acid aerosol would have nearly the same aerosol volume. One expects this assumption to give a somewhat lower aerosol volume than seen by the EAA because compounds other than ammonium sulfate and water are likely to be in the aerosol.

Table 6 compares the plume excess aerosol volume measured by the EAA and that calculated from the plume excess sulfate data and the assumption above. The table only includes measurements taken at or very close to the same time.

Before forming the ratios in Table 6 the plume excess aerosol concentrations were normalized by the average SO_2 concentration at the points of measurement and the plume excess sulfate concentrations were normalized by the average SO_2 concentration during the filter sample periods. This procedure should cancel the effect of the different plume concentrations sampled by two methods. Some scatter will still result since the filter measurements average continuously through the plume while the plume aerosol concentration is the average of measurements made at 1 to 4 points in the plume.

Table 6 shows that much more sulfate was seen by the filter measurements than can be accounted for by the EAA data; whereas, one would expect to see somewhat more aerosol than sulfate. The geometric mean ratio (after throwing out numbers greater than 10 and less than 0.5) is 2.8 with a geometric standard deviation of 1.22. (The geometric standard deviation of the individual points is 2.4.) We know of no obvious explanation for the high sulfate to aerosol ratio since the ratio is larger than the probable bias from any one source. Possible factors which may contribute to this discrepancy are:

- 1) Sampling Bias: Sulfate per unit SO_2 usually forms more rapidly where the plume is dilute. Since the filter samples are taken across the entire plume and the EAA samples were taken, usually, in higher concentration areas, the filter samples may have collected proportionally higher sulfate values. Very limited data are available to estimate this bias, but it is probably less than a factor of 1.4. Data close to the source would not have this bias.
- 2) Aerosol Hydration: Under dryer conditions, ammonium sulfate will be present as a solid particle instead of a deliquesced drop. Ammonium bisulfate and sulfuric acid will lose water to a lesser extent. Assuming a dry aerosol would reduce the ratios in Table 6 by about a factor of 2.5. However,

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TABLE 6. COMPARISON OF SULFATE AND AEROSOL MEASUREMENTS

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Sample Time	Distance (km)	Sulfate As Aerosol Volume Measured * Volume by EAA
8/17 Morning	0.5 3 9	3.8 3.1 5.4
8/17 Late Afternoon	.5 3 7	0 2 30
8/19 Early Morning	0.5 9 24 25 45 47 75	.58 2.3 4.6 3.3 16 9.1 8.8
8/19 Late Afternoon	9-13 58	58 4.3
8/21 Morning	15-20 15 20 30	4.1 0.9 <0 1.7
8/23 Morning	11-14 50	16 -0.2
8/23 Afternoon	13 50 70	1.1 24 6.7
8/25 Early Morning	0.5 0.5 8 20	0.58 8.4 <0 <0
8/25 Late Morning	45 45 50	3.9 .50 1.2

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* Plume excess including primary emissions.

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relative humidity measured during the study indicated wet aerosol.

- 3) Bias in Sulfur Measurements: The RSP-IC data showed significantly more sulfur than the Two-Mass data. The Two-Mass FPD system seems more likely biased low than the RSP-IC to be biased high. If the Two-Mass FPD data are correct, the ratios in Table 6 would be reduced by a factor of about 1.5. However, the sulfur conversion rates as calculated are reasonable compared to work of others.
- 4) EAA Bias: The EAA measures total aerosol volume typically to 30 percent accuracy. Usually it will overpredict aerosol concentrations in channels 9 and 10 and a correction was included during data reduction. The exclusion of channel 10 from the total aerosol volume may have overcorrected for this error and possibly resulted in the EAA data being low by a factor of about 1.2.

← A combination of the above errors could account for the high sulfate to aerosol ratios in Table 6 and we have no good evidence to point to any one of them.

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SECTION 6

PRIMARY SULFURIC ACID

Since sulfuric acid has a very low vapor pressure under typical ambient conditions, nearly all of this acid in the flue gas will condense into aerosol soon after the plume leaves the stack. Other non-sulfate compounds in the vapor state in the flue gas are not likely to have high enough concentrations to form significant aerosol concentrations. Therefore, the sulfuric acid concentrations in the stack flue gas can be reasonably well estimated by multiplying the plume excess aerosol volume by the plume dilution (the ratio of the stack to plume SO₂ concentrations) and subtracting the source fly ash and water absorbed by the acid. Because a small amount of acid produces large quantities of submicron aerosol, small quantities of acid can be detected. The following sections show the results of the analysis outlined above applied to the Widows Creek data.

MEASUREMENTS, CALCULATIONS, AND ASSUMPTIONS

Flue gas submicron fly ash and SO₂ concentrations required for the following analysis were not specifically measured in this study; we obtained them from other data.

Flue Gas Submicron Fly Ash Concentrations

Studies by Meteorology Research, Inc. (MRI) (Markowski et al., 1980, and in preparation; Ensor et al., 1979, 1981, and in preparation) at boilers burning a wide variety of coals show that flue gas submicron volume concentrations vary between 6 to 32 mm³ fly ash per cubic meter flue gas with the submicron concentration approximately linearly related to NO concentrations. (All source flue gas concentrations in this section are dry normal and corrected to 3 percent O₂.) Measurements by Radian (Balfour et al., 1981; Balfour, 1981) give NO concentrations in all three units between 200 and 450 ppm. Although these measurements were made about a year after this study, NO concentrations are not likely to increase much since they depend mostly on boiler firing which is usually fixed by boiler design. The lower NO concentrations, about 200 ppm for Units 7 and 8, seem unrealistically low. MRI's data indicate boiler flue gas submicron concentrations of about 10 mm³/m³ for NO concentrations of about 400 ppm, and perhaps 5 mm³/m³ if the lower NO figures are real.

The control devices on Units 7 and 8 collect submicron aerosol rather poorly, so that stack concentrations are probably about 1/2 of the boiler

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concentrations, or about $5 \text{ mm}^3/\text{m}^3$. The high efficiency ESP on Units 1-6 should remove at least 90 percent of the submicron fly ash.

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Flue Gas SO₂ Concentrations

SO₂ measurements were made during this study by Midwest Research, Inc. (MWR) (Maxwell, 1978) on Unit 8 only by continuous monitors belonging to the Widows Creek Steam Plant and about a year later by Radian (Balfour et al., 1981). Unfortunately most of MWR's SO₂ data are unrealistically high. Daily average plant SO₂ concentrations for Unit 8 uncorrected for excess air are given in the TVA data volume (Meagher, 1978b); however, MWR and Radian's data show high O₂ concentrations so that dilution by ambient air is large (typically factors between 1.5 and 2.2) and must be corrected for. Flue gas SO₂ can be calculated from the coal composition to at least 20 percent accuracy and this method is probably most accurate. Coal composition during this study is in the TVA data volume (Meagher, 1978b).

Coal composition gives flue gas SO₂ concentrations for Unit 7 and Units 1-6 of 3200 and 645 ppm, respectively. These values are within 10 percent of continuous monitor values corrected to 3 percent O₂. The SO₂ concentration at the scrubber outlet of Unit 8 corrected for dilution is estimated to be 367 ppm based on the plant's 8/17 daily SO₂ average, and the excess air inferred from MWR measurements (MWR's O₂ concentrations agree well with Radian's). Excursions are possible from these average values.

Aerosol Composition

It is necessary to know the fraction of sulfuric acid in the downwind aerosol and its density must be estimated to calculate the amount of acid at stack conditions. The near source plume excess aerosol is probably mostly sulfuric acid and water. At a typical relative humidity of 70 percent, the data of Nair and Vohra (1975) and Carabine and Maddock (1976) indicate that the aerosol will be about 34 percent acid by weight with a specific gravity of 1.24. Under these conditions, 1 ppm of H₂SO₄ is equivalent to aerosol concentrations of $10.4 \text{ mm}^3/\text{m}^3$.

PRIMARY SULFURIC ACID

Table 7 summarizes the results of this analysis: sulfuric acid is indicated in all units, although zero acid is within the error limits for Unit 8. Table 7 shows the most likely acid concentration and the 95 percent confidence limits based on our assessment of possible errors. We assumed that the plume excess aerosol volumes from the EAA measurements were accurate to a factor 1.5. The column which shows the percentage of sulfuric acid in the primary aerosol indicates that nearly all of the primary aerosol from Units 7 and 1-6 is sulfuric acid.

Unit 8 Sulfuric Acid

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The average Unit 8 plume excess concentrations of $0.013 \text{ mm}^3/\text{m}^3$ aerosol and 293 ppb SO₂ indicate an undiluted aerosol concentration, i.e., flue gas concentration, of $16.3 \text{ mm}^3/\text{m}^3$. Since the fly ash concentration is about

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TABLE 7. PRIMARY FLUE GAS SULFURIC ACID

	Flue gas ¹ SO ₂ (ppm)	Sulfuric Acid (ppm)		Calculated Fraction of Fine Primary Aerosol That is Sulfate (%)	Average Plume Excess ³ SO ₂ Aerosol (mm ³ /m ³)		Distance (km)
		Calculated	Maximum ²		SO ₂ ppm	Aerosol (mm ³ /m ³)	
Unit 8	367	1.1	3.0	0	0.293	0.013	0.5
Unit 7	3200	8.0	17	2.4	0.634	0.018	0.5
Units 1-6 ⁴	645	2.6	6.2	1.0	0.142	0.0061	20

- ¹Corrected to 3 percent O₂.
²Approximate 95 percent confidence limits.
³In mixed plume.
⁴Only one size distribution in plume.

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5 mm³/m³, most of the aerosol is probably sulfuric acid and is equivalent to 1.1 ppm sulfuric acid. This amount is normally within the noise of source sulfuric acid measurement methods. Figure 8 shows the plume excess aerosol size distribution compared to the predicted fly ash distribution. The large difference in shape must be caused by additional aerosol formation outside of the stack.

Although unlikely, boiler submicron concentrations as high as 32 mm³/m³ cannot be ruled out. Conservatively assuming only 50 percent collection efficiency in the ESP and scrubber, all the Unit 8 source aerosol could be accounted for by fly ash. Therefore, we have included zero acid in the confidence limits. We have estimated a possible error of a factor of 1.5 in the scrubber outlet SO₂ concentrations. That error and aerosol measurement error (a factor of 1.5 is possible) are the main sources of error. We estimate the maximum sulfuric acid concentration to be 3.0 ppm. Most of the MWR's sulfuric acid measurements (Maxwell, 1978), 1.5 to 18 ppm, are above our upper limit. Radian's (10/79) two acid measurements were 2.2 and 3.9 ppm (Balfour et al., 1981).

The MRI data above were from 8/17. The plume excess aerosol volume to SO₂ ratios on two other flights near Unit 8 when Unit 7 was down were within 10 percent of the values measured on 8/17.

Unit 7 Sulfuric Acid

No flights were made when Unit 8 was down, so only the mixed plumes from Units 7 and 8 were sampled. Since the plume from Unit 8 was studied separately and the power levels of Units 7 and 8 during sampling were known (Meagher, 1978b), Unit 8's contribution can be subtracted and the aerosol to SO₂ ratio for Unit 7 alone calculated. This analysis indicates a Unit 7 flue gas (i.e. no dilution) submicron aerosol concentration of 88 mm³/m³, far above any reasonable fly ash concentrations. Subtracting the expected fly ash, 5 mm³/m³, leaves an acid concentration of 8 ppm. Figure 9 shows the plume excess aerosol distribution at 0.5 km and the expected fly ash distribution. Note the large difference in shape and concentration.

The error analysis is somewhat complicated by the mixed plumes. We have assumed that the plumes are completely mixed; however, the results are insensitive to the mixing ratio unless less than 20 percent of the sampled plume is from Unit 7. (If the plume is only 20 percent from Unit 7, we will overestimate its acid concentration by 30 percent.) Since our data are the average of about 8 different points in the plume, we do not think mixing is a major source of error.

We estimate the 95 percent confidence limits for the fine particle primary sulfuric acid as 17 and 2.4 ppm. For the minimum we assumed the plume to be 25 percent from Unit 7 and, as before, a submicron aerosol concentration of 16 mm³/m³. We assume in both cases aerosol volume errors to be a factor of 1.5. We assume the SO₂ concentration to be better known than for Unit 8 and uncertain by a factor of 1.2.

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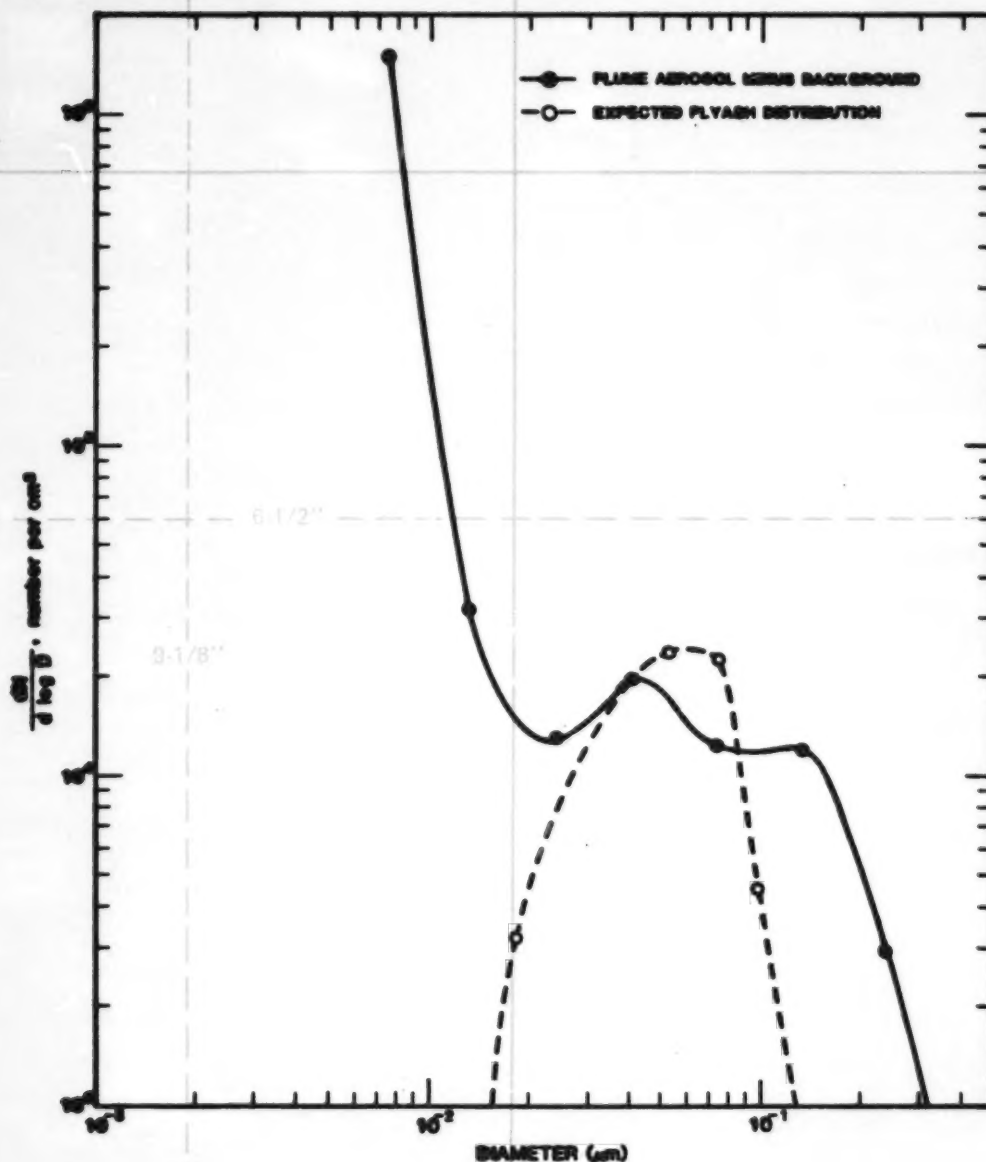


Figure 8. Plume excess aerosol distribution from Unit 8 at 0.5 km downwind compared to expected fly ash distribution. Data were taken on August 17, 1978 at 9 a.m.

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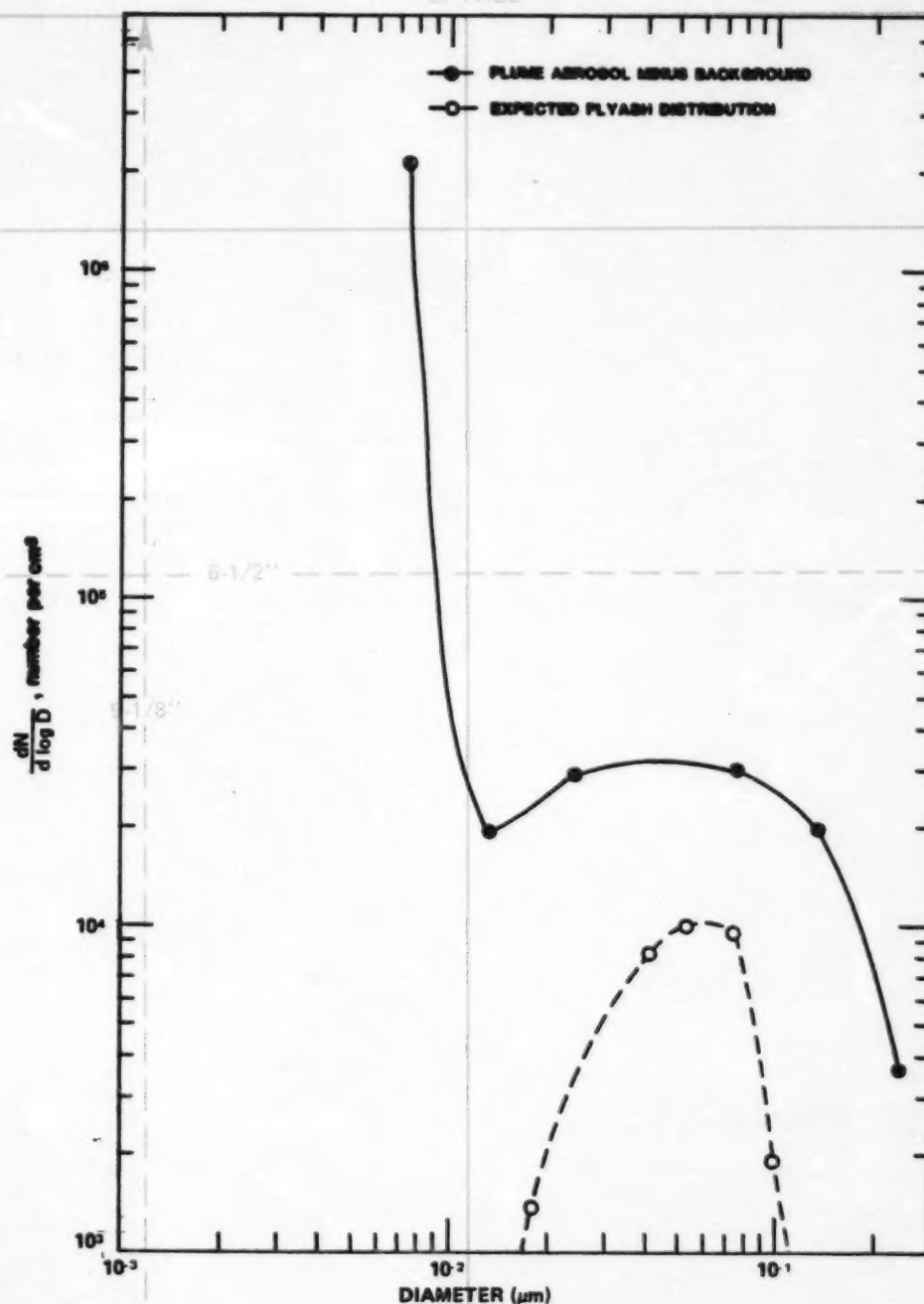


Figure 9. Plume excess aerosol distribution from Units 7 and 8 at 0.5 km downwind compared to expected fly ash distribution. Difference is probably condensed sulfuric acid. Data were taken on August 25, 1978 at 7:30 a.m.

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MWR measured sulfuric acid concentrations between 1.2 and 28 ppm at the Unit 8 scrubber inlet during the study. Since the two boilers are the same and burn the same coal, the acid concentrations at the boiler outlet should be nearly the same. MWR's data are in rough agreement with our results. However, about 10 ppm ammonia was added to the Unit 7's flue gas to raise its ESP collection efficiency. The treatment probably results in 5 to 15 ppm sulfuric acid collected in the ESP as ammonium sulfate or bisulfate.

Radian in October 1979 measured 0.7, 2.0 and 2.1 ppm sulfuric acid in Unit 7. These values seem low compared to our measurements, even though the coal burned during Radian's study had 35 percent less sulfur. Although, our analysis cannot differentiate between sulfuric acid and ammonium sulfate or bisulfate aerosols, the controlled condensation method used by Radian is also sensitive to these sulfate salts.

Units 1-6 Sulfuric Acid

On the morning of August 25 the highest and most southerly portion of the plume at 20 km appeared to be solely from Units 1-6: convection had not started and the plume from Units 1-6 was blown more southerly because of the wind shear above the stacks of Units 7 and 8. The absolute position of the plume which we identified as from Units 1-6 and also its position relative to the plume from Units 7 and 8 agreed well with the wind data. MRI measured one size distribution in the plume from Units 1-6.

The aerosol measured corresponded to a flue gas concentration of $27 \text{ mm}^3/\text{m}^3$ or a sulfuric acid concentration of 2.6 ppm. No correction was made for submicron fly ash since nearly all of the submicron fly ash should be collected in Units 1-6 high efficiency ESP. Since the measurement was 20 km downwind the aerosol is probably mostly ammonium sulfate or bisulfate. We estimate flue gas acid 95 percent confidence limits of 1.0 and 6.2 ppm. These limits include a factor of 2 uncertainty in the aerosol volume since only one size distribution measurement was made. Although some of the aerosol may possibly have formed from photochemical reactions, we think the amount is small since: 1) the plume was airborne only about 50 minutes fairly early in the morning (from about 7:40 to 8:30 a.m.), 2) a significant nuclei mode was absent, and 3) the plume was fairly concentrated.

COMPARISON OF THE SCRUBBED AND UNSCRUBBED UNITS

The sulfuric acid concentration in Unit 8's flue gas is about one eighth of that from Unit 7. Since the major difference between the two units is the scrubber on Unit 8, most of the acid must be removed in the scrubber.

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SECTION 7

GAS CHEMISTRY

Marked changes in O_3 , NO_x , and NO_2 concentrations were seen at times in the plume. O_3 bulges were common when the plume was dilute, NO_2 rapidly disappeared from the plume relative to SO_2 , and excess concentrations were seen near the source.

OZONE BULGES

Table 8 lists all flights and shows when ozone bulges were measured. On flights when no ozone bulge was seen, only an entry for the maximum distance from the plant is shown. When an ozone bulge was seen, data are included at the largest distance an ozone bulge was not seen. The data show that ozone bulges were seen on all afternoon flights 30 km or more downwind of the plant. On August 19 the beginning of the bulge could be seen as close as 9 km as an insufficient ozone deficit in the plume. The table indicates the major variables affecting in the ozone bulges are sunlight intensity (i.e., time of day) and plume dilution. Ozone bulges were not observed until the plume was diluted to about 50 ppb SO_2 or less. The ozone bulges are correlated with the NO_x loss described below. Our data indicate that ozone bulges are more the rule rather than the exception on convective days and that they form rather soon after the flue gas leaves the stack.

Comparison of Ozone Bulges in Scrubbed and Unscrubbed Plumes

Although the plumes were well mixed by convection, the amount of SO_2 in the plume varied considerably from day to day. About 2.5 to 3 times as much SO_2 was being released on August 19 and August 25 when Unit 7 was running at 290 to 400 MW compared to August 23 when Unit 7 was down. Units 1-6 and Unit 8 were running under relatively constant conditions during all the flights. In spite of the large change in SO_2 , the ozone bulges on August 23 and August 25 are nearly identical. The smaller bulge seen on August 19 is likely the result of the shorter travel time and lower plume dilutions. The presence of the plume from Unit 7 which contains higher concentrations of SO_2 does not appear to have a large influence on ozone formation.

NO_x DEPLETION

At distances beyond 30 km in the afternoon, very little NO_x could be seen in the plume. The Monitor Labs chemiluminescent NO/NO_x monitor is sensitive to gaseous HNO_3 and PAN so that these species appeared to be absent also. HNO_3 and PAN are the expected reaction products of NO_x . The

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TABLE 8. OZONE BULGES

Date	Time Flight	Power (MW)			Distance* (km)	Ozone Bulge?	Ozone (ppb)		Ave. Plume SO ₂ (ppb)	Travel Time (hrs)
		Units	1-6	7 8			Background	Excess		
8/17	Morning 1130	500	0	320	9	No			35	0.6
8/17	Late Afternoon 1845	520	0	320	7	No			35	0.86
8/19	Morning 900	441	305	245	24	No			60	1.6
	1030				47	Yes	58	5	35	3.4
	1100				75	Yes	60	8	15	5.1
8/19	Afternoon 1605	686	400	230	9	Yes ⁺	74	2 ⁺	50	0.43
	1612				13	Yes ⁺	68	5 ⁺	50	0.7
	1625				17	Yes	NA ^{**}	5 ^{**}	25	0.83
	1710				30	Yes	78	5	20	1.9
8/21	Morning 0910	520	295	230	30	No			50	1.7
8/22	Early Morning 0810	551	0	215	10	No			25	NC
8/23	Morning 1030	770	0	245	11	No			80	0.85
	1235				50	Yes	88	20	20	4.1
8/23	Afternoon 1520 ⁺⁺	780	0	245	70	Yes	82	24	3	6.6
	1730				50	Yes	84	44	7	4.8
	1830				15	No			30	1.4
8/25	Early Morning 0830	750	255	285	20	No				
8/25	Mid- Morning 1055	760	290	250	45	? ^{***}		***	20	3.5
	1230				46	Yes	102	26	12	2.8
	1310				46	Yes	96	36	4	2.8

NC - not computed.

NA - not available.

* - when no O₃ bulge is seen, maximum traverse distance is shown.

+ - O₃ did not exceed background but O₃ deficit was too small by amount shown under excess column.

** - data taken in an orbit. When SO₂ below 15 ppb, O₃ increases as much as 5 ppb as SO₂ increases.

++ - 15 to 25 percent reduction in sunlight from 1200 to 1500.

*** - no deficit or excess ozone seen as SO₂ varied in this orbit.

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NO_x appeared to be lost much more rapidly than SO₂. Only the data on August 23 were good enough to make a quantitative estimate of NO_x removal.

On August 23 Unit 7 was down. Assuming the Unit 1-6 NO_x/SO₂ ratio was 2/5 of Unit 8 (i.e., assuming Units 1-6 had the same NO_x concentration in the flue gas and 5/2 the SO₂ concentration since Units 1-6 are unscrubbed but burn only 1 percent sulfur coal) and using the measured Unit 8 NO_x/SO₂ ratio of 0.7, NO_x/SO₂ in the mixed plumes is calculated to be 0.33. This estimate is likely smaller than actual because: (1) Radian measured (October 1979) NO_x in Units 1-6 about twice Unit 8, and (2) NO_x/SO₂ measured at about 11 km on August 23 was between 0.69 and 1.4.

At 50 km (4.1 hours travel time) on August 23, the measured NO_x/SO₂ ratio was 0.14. The total conversion was, therefore, 58 percent, an average of 14 percent per hour. This value is a lower limit because of the conservative estimate discussed above. Assuming a mixed plume NO_x/SO₂ ratio of 0.69 (that measured at 11 km) gives a total conversion of 80 percent or an average rate of 25 percent per hour. These results are from a plume released about 8:30 a.m. when sunlight was about 1/3 of its peak value. The instantaneous rates from 11 p.m. to 2 p.m. are likely to be considerably higher than the average values because of increased sunlight intensity.

NEAR SOURCE NO₂

NO and NO_x measurements near the source (0.5 to 11 km) showed that 21 ± 4 percent of the source NO was converted to NO₂ by some other reaction other than the reaction with ambient ozone. The reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ can account for 5 to 6 percent conversion and 2 to 3 percent may be accounted for by primary emissions. (Unit 8 emits no NO₂ since it is completely scrubbed. Flue gas NO₂ concentrations relative to NO measured by Radian in October 1979 were 3, 4, and 0 percent for Units 1-6, 7, and 8 respectively.) Thus about 12 percent of the observed NO₂ is unexplained. The possibility that this unexplained NO₂ is due to measurement error can not be ruled out.

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